United States Patent [19]

Charkoudian

[11] **3,816,126**

[45] **June 11, 1974**

[54] **NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES**

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

[22] Filed: **Sept. 11, 1972**

[21] Appl. No.: **287,629**

[52] **U.S. Cl.** ..... **96/3,** 96/29 D, 96/66 R, 96/76 R, 96/77

[51] **Int. Cl.** **G03c 7/00,** G03c 5/54, G03c 5/30, G03c 1/48, G03c 1/40

[58] **Field of Search** ..... 96/3, 76 R, 95 R, 77, 66 R, 96/29 D

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2,983,606	5/1961	Rogers	96/3
3,009,958	11/1961	Green et al.	96/66 R
3,186,843	6/1965	Haas	96/66 R
3,246,988	4/1966	Porter et al.	96/66 R
3,415,646	12/1968	Land	96/3
3,577,236	5/1971	Fix	96/3
3,639,126	2/1972	Verelst et al.	96/66 R
3,650,749	3/1972	Willems et al.	96/95 R

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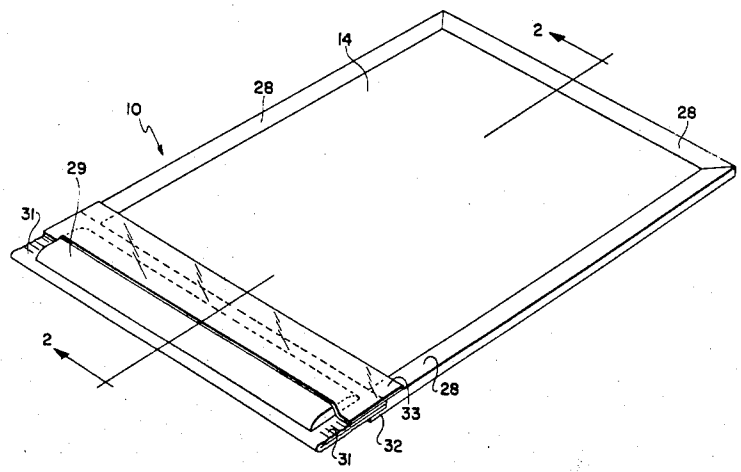
Lee and James, "Superadditivity in Photographic Development by Substituted Hydroquinones Used with Phenidone," Photo. Science and Engrg., Vol. 6, No. 1, Jan.–Feb. 1962, pp. 32–38.

Primary Examiner—Ronald H. Smith
Assistant Examiner—Richard L. Schilling

[57] **ABSTRACT**

The present invention is directed to a photographic film unit adapted to provide, by diffusion transfer processing, selective dye image recordation of incident actinic radiation as a function of the point-to-point degree of photosensitive element exposure, which film unit includes a plurality of layers including a photosensitive silver halide layer having associated therewith diffusion transfer process dye image-forming material; and a silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the precursors thereof, and a layer adapted to receive dye image-forming material diffusing thereto; and to specified diffusion transfer processes employing such film units.

22 Claims, 7 Drawing Figures



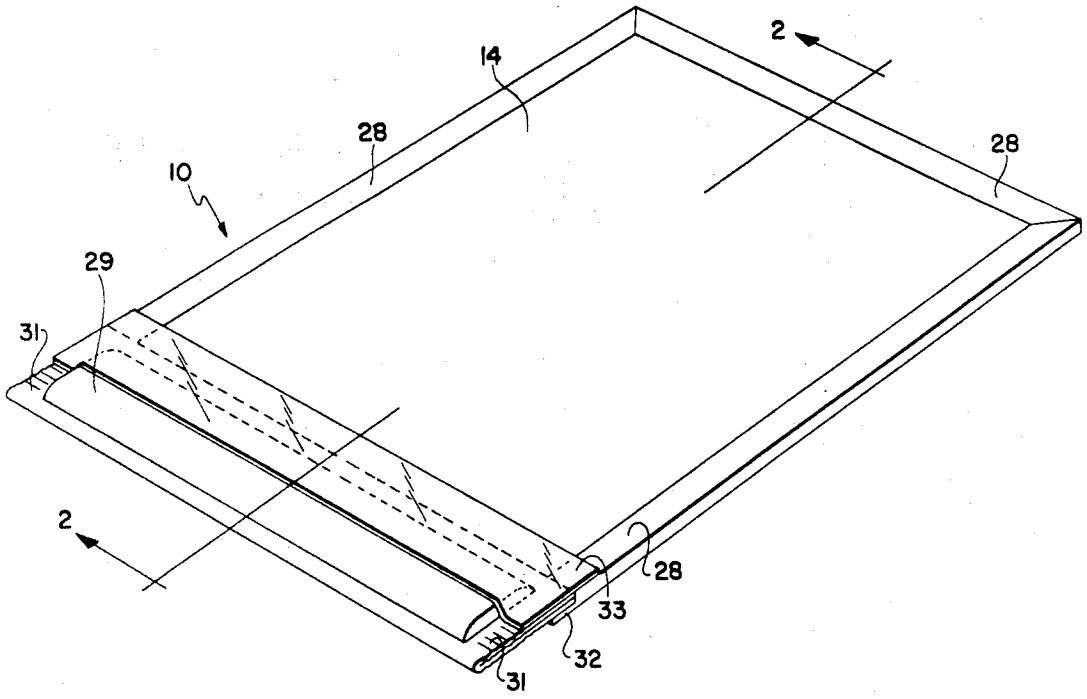


FIG. 1

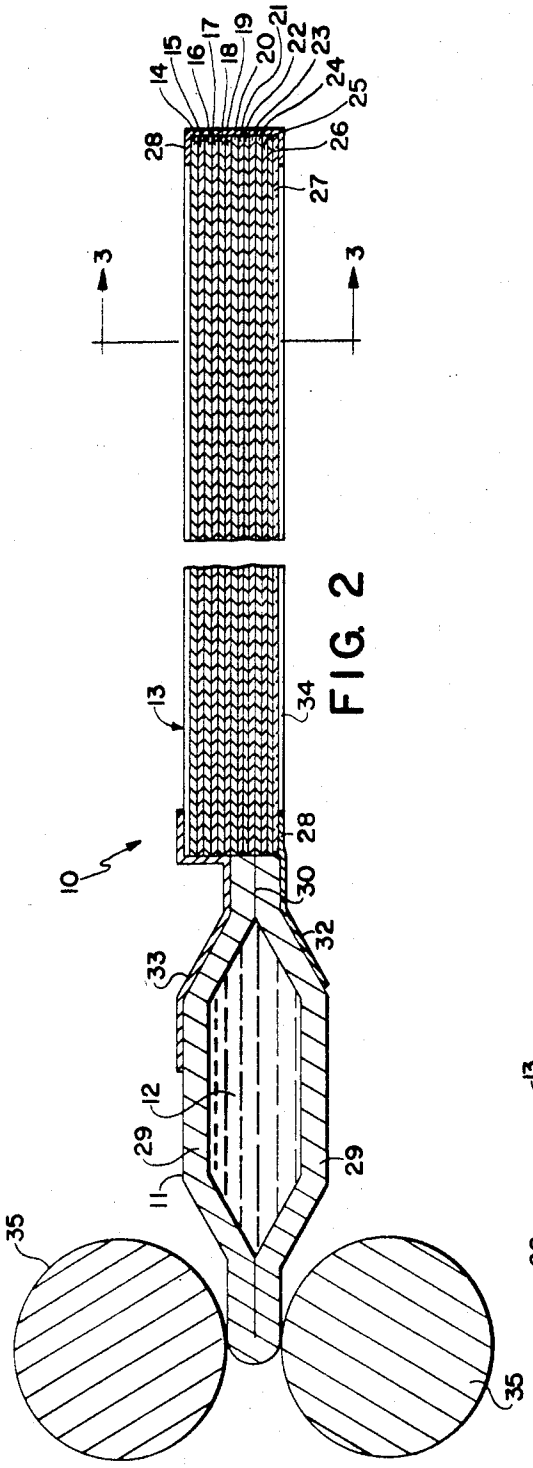

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FIG. 2

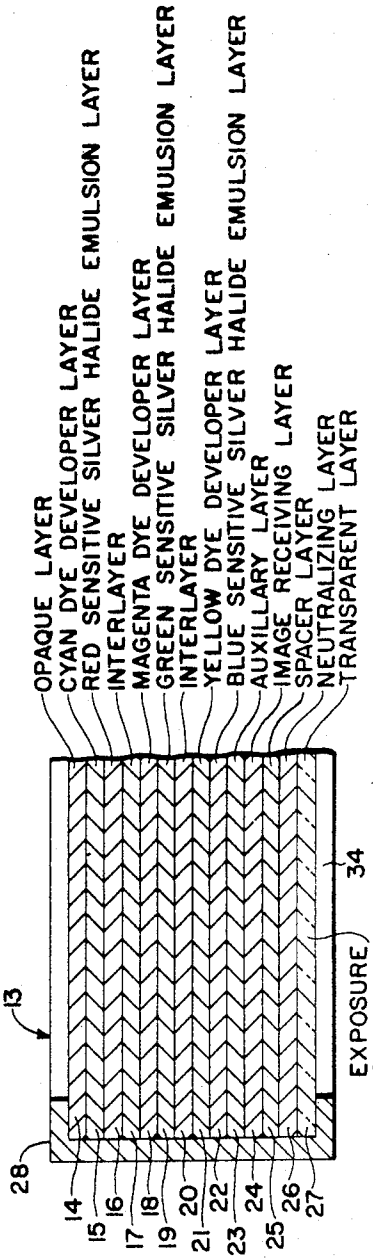

OPAQUE LAYER
CYAN DYE DEVELOPER LAYER
RED SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
MAGENTA DYE DEVELOPER LAYER
GREEN SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
YELLOW DYE DEVELOPER LAYER
BLUE SENSITIVE SILVER HALIDE EMULSION LAYER
AUXILLARY LAYER
IMAGE RECEIVING LAYER
SPACER LAYER
NEUTRALIZING LAYER
TRANSPARENT LAYER
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EXPOSURE SURFACE
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FIG. 3

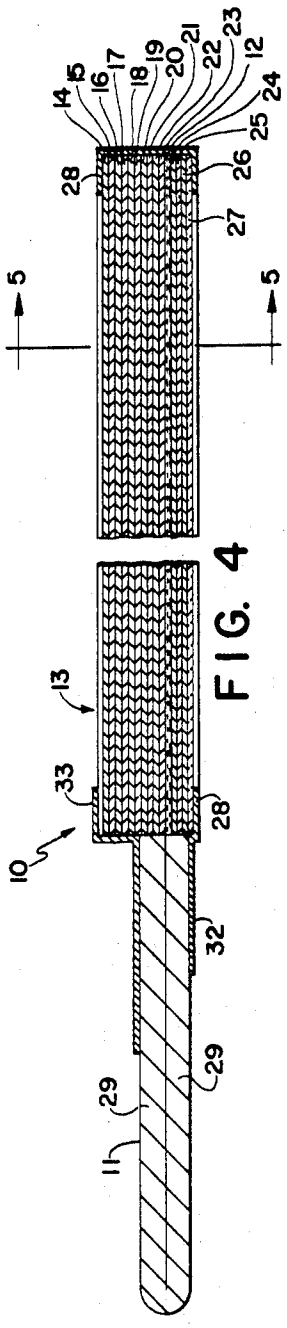

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FIG. 4

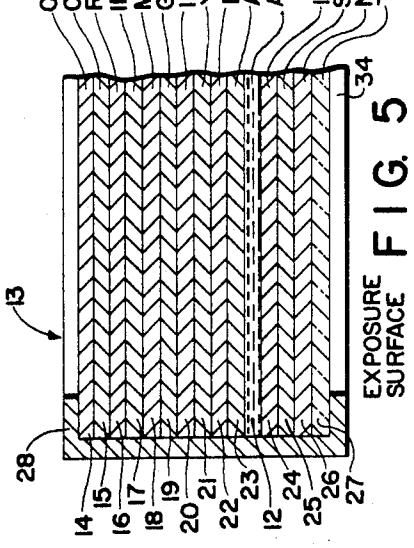

OPAQUE LAYER
CYAN DYE DEVELOPER LAYER
RED SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
MAGENTA DYE DEVELOPER LAYER
GREEN SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
YELLOW DYE DEVELOPER LAYER
BLUE SENSITIVE SILVER HALIDE EMULSION LAYER
AUXILLARY LAYER
ALKALINE PROCESSING COMPOSITION CONTAINING
IMAGE RECEIVING LAYER
SPACER LAYER
NEUTRALIZING LAYER
TRANSPARENT LAYER
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EXPOSURE SURFACE

FIG. 5

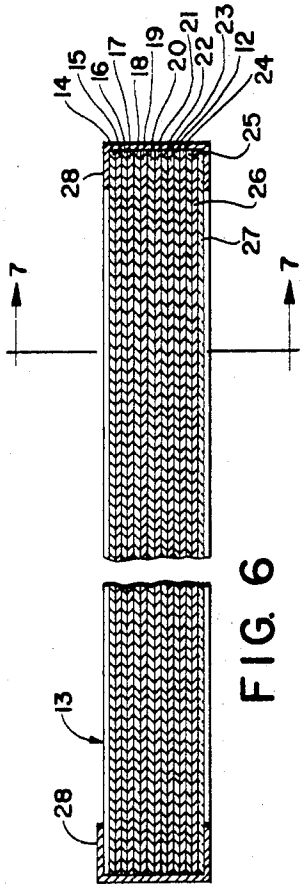

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FIG. 6

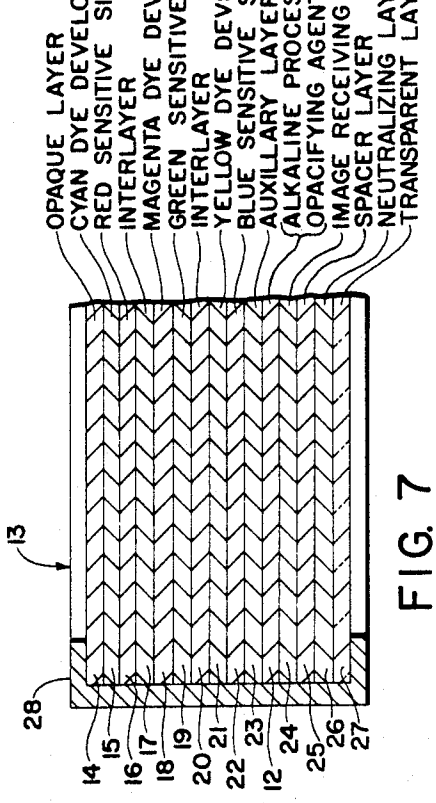

OPAQUE LAYER
CYAN DYE DEVELOPER LAYER
RED SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
MAGENTA DYE DEVELOPER LAYER
GREEN SENSITIVE SILVER HALIDE EMULSION LAYER
INTERLAYER
YELLOW DYE DEVELOPER LAYER
BLUE SENSITIVE SILVER HALIDE EMULSION LAYER
AUXILLARY LAYER
ALKALINE PROCESSING COMPOSITION CONTAINING OPACIFYING AGENT
IMAGE RECEIVING LAYER
SPACER LAYER
NEUTRALIZING LAYER
TRANSPARENT LAYER
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FIG. 7

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to providing new and improved diffusion transfer process photographic film units adapted to provide, as a function of the point-to-point degree of photoexposure, by diffusion transfer processing a dye transfer image.

2. Description of Prior Art

As disclosed in U.S. Pat. No. 3,415,644, a composite photosensitive structure, particularly adapted for reflection type photographic diffusion transfer color process employment, which comprises a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of its associated silver halide emulsion's exposure to incident actinic radiation; a polymeric layer adapted to receive solubilized dye image-providing material diffusing thereto; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition from the first pH to a second pH at which the dye image-providing material is substantially nondiffusible; and a dimensionally stable transparent layer, may be exposed to incident actinic radiation and processed by interposing, intermediate the silver halide emulsion layer and the reception layer, an alkaline processing composition possessing the first pH and containing opacifying agent, which may reflect incident radiation, in a quantity sufficient to mask dye image-providing material associated with the silver halide emulsion.

In a preferred embodiment, the composite photosensitive structure includes a rupturable container, retaining the alkaline processing composition having the first pH and opacifying agent, fixedly positioned extending transverse a leading edge of the composite structure in order to effect, upon application of compressive pressure to the container, discharge of the processing composition intermediate the opposed surfaces of the reception layer and the next adjacent silver halide emulsion.

The liquid processing composition, distributed intermediate the reception layer and the silver halide emulsion, permeates the silver halide emulsion layers of the composite photosensitive structure to initiate development of the latent images contained therein resultant from photoexposure. As a consequence of the development of the latent images, dye image-providing material associated with each of the respective silver halide emulsion layers is individually mobilized as a function of the point-to-point degree of the respective silver halide emulsion layer's photoexposure, resulting in imagewise distributions of mobile dye image-providing materials adapted to transfer, by diffusion, to the reception layer to provide the desired transfer dye image. Subsequent to substantial dye image formation in the reception layer, a sufficient portion of the ions of the alkaline processing composition transfers, by diffusion, to the polymeric neutralizing layer to effect reduction in the alkalinity of the composite film unit to the second pH at which dye image-providing material is substantially

nondiffusible, and further dye image-providing material transfer is thereby substantially obviated.

The transfer dye image is viewed, as a reflection image, through the dimensionally stable transparent layer against the background provided by the opacifying agent, distributed as a component of the processing composition, intermediate the reception layer and next adjacent silver halide emulsion layer. The thus-formed opacifying stratum effectively masks residual dye image-providing material retained in association with the silver halide emulsion layer subsequent to processing.

In U.S. Pat. No. 3,415,646, the dimensionally stable layer of the film unit next adjacent the photosensitive silver halide layer or layers is disclosed to be transparent to incident actinic radiation and as disclosed in U.S. Pat. No. 3,415,645, in such instance the opacifying agent may be initially disposed in the film unit intermediate the reception layer and next adjacent silver halide layer.

As disclosed in U.S. Pat. No. 3,615,421 of Edwin H. Land, issued Oct. 26, 1971, and the copending U.S. patent application Ser. No. 3,646 of Sheldon A. Buckler, filed Jan. 19, 1970, now U.S. Pat. No. 3,661,585 issued May 9, 1972, the opacifying component of the film unit may optionally be initially disposed as a preformed processing composition permeable layer, intermediate the reception layer and next adjacent silver halide layer, in a concentration which prior to photoexposure is insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the film unit's silver halide emulsion layers, and in the copending U.S. patent application Ser. No. 43,742 of Edwin H. Land, filed June 5, 1970, now U.S. Pat. No. 3,647,435 issued Mar. 7, 1972 the opacifying component of the film unit may optionally be initially formed in situ, intermediate the reception layer and next adjacent silver halide layer, during photographic processing of the film unit.

In the copending U.S. patent applications of Edwin H. Land, Ser. No. 786,352, filed Dec. 23, 1968, and Ser. No. 43,782, filed June 5, 1970, the opacifying component is disclosed to optionally comprise a light-absorbing reagent such as a dye which is present as an absorbing species at the first pH and which may be converted to a substantially non-absorbing species at the second pH, and in U.S. Pat. Nos. 3,473,925 and 3,573,042 and the U.S. Pat. of Terry W. Milligan and Richard W. Young, No. 3,576,626 issued Apr. 27, 1971, opacifying and reflecting component, respectively, may be individually interposed intermediate the silver halide layer and reception layer by selective distribution from a composite or a plurality of rupturable containers.

In U.S. Pat. No. 3,573,043, the polymeric neutralizing layer is disclosed to be optionally disposed intermediate the dimensionally stable opaque layer and next adjacent essential layer, i.e., next adjacent silver halide/dye image-providing material component, to effect the designated modulation of film unit's environmental pH; the U.S. Pat. No. 3,576,625 of Edwin H. Land, issued Apr. 27, 1971, discloses the employment of particulate acid distributed within the film unit to effect the modulation of the environmental pH, and U.S. Pat. No. 3,573,044 discloses the employment of processing

composition solvent vapor transmissive dimensionally stable layers to effect process modulation of dye transfer as a function of solvent concentration.

Where desired, the film unit may also be constructed in accordance with the disclosure of U.S. Pat. No. 3,594,165 issued July 20, 1971, to Howard G. Rogers and U.S. Pat. No. 3,594,164 issued July 20, 1971, to Howard G. Rogers to comprise a composite photosensitive structure including a transparent dimensionally stable layer carrying a reception layer, a processing composition permeable opaque layer and a photosensitive silver halide layer and the film unit may include a separate dimensionally stable sheet element adapted to be superposed on the surface of the photosensitive structure opposite the dimensionally stable layer and may further include means such as a rupturable container retaining processing composition for distribution of a processing composition intermediate the sheet and photosensitive structure to effect processing. As further disclosed in the last-cited applications, in structures wherein the receptor is positioned next adjacent the transparent layer or the processing composition and/or the sheet is to be separated from the remainder of the film unit subsequent to processing, the latter elements may optionally include opacifying component.

As disclosed in the U.S. Pat. No. 3,620,724 issued Nov. 16, 1971, to Edwin H. Land, the dimensionally stable layer referred to may be opaque and in which instance the photosensitive silver halide layer is positioned next adjacent the opaque support layer and the opacifying component of the film unit's processing composition permeable opaque layer will be disposed in the unit in a concentration insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses an opacifying capacity effective to mask residual dye image-providing material retained associated with the silver halide layer, and as disclosed in the copending U.S. Pat. application Ser. No. 43,741 of Edwin H. Land, filed June 5, 1970, now U.S. Pat. No. 3,647,434 issued Mar. 7, 1972, the opacifying agent may be optionally formed in such film unit, in situ, during processing of the unit.

U.S. Pat. No. 2,983,606 also discloses the employment of a combination of a dye developer and one or more silver halide developing agents which are not dye developers, which may act to accelerate or initiate development. Such added developing agents are referred to as an auxiliary or cooperative developing agent. The auxiliary developing agents provide cleaner highlights and better intermediate tones. The auxiliary developing agent may be disposed in the processing composition or one or more layers of the photosensitive element, e.g., in the silver halide emulsion layer or in the layer containing the dye developer.

The present invention is directed to film units processed with a novel class of auxiliary developers.

SUMMARY OF THE INVENTION

The present invention is directed to a new and improved, preferably integral negative/positive, diffusion transfer process photographic film unit adapted to provide, by diffusion transfer processing, photographic color image reproduction as a function of exposure of such film unit to incident actinic radiation.

The film unit assemblage construction to be employed in the practice of the present invention preferably comprises a film unit of the general type set forth in aforementioned U.S. Pat. Nos. 3,415,644; 3,415,645; and 3,415,646; 3,473,925; 3,573,042; 3,573,043; 3,573,044; and copending U.S. Patent applications Ser. Nos. 786,352; 3,691; 43,741; 43,742; and 43,782 and also in U.S. Pat. Nos. 3,615,421; 3,576,625; 3,576,626; 3,620,724; 3,594,165; 3,594,164; 2,983,606; and 3,345,163; and will include one or more photosensitive silver halide layers having associated therewith dye image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; and an auxiliary developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-ti-butyl hydroquinone; durohydroquinone; and the precursors thereof, e.g., the alkyl esters, preferably the haloalkyl esters thereof; a layer adapted to receive image-forming material diffusion thereto; a dimensionally stable layer transparent to incident actinic radiation; and means for interposing, intermediate the silver halide layers and the reception layer, opacifying agent and a processing composition, and, in a particularly preferred embodiment, a processing composition possessing a first pH at which the dye image-forming material is diffusible during processing and means for modulating the pH of the film unit from the first pH to a second pH at which the dye image-forming material is substantially non-diffusible subsequent to substantial dye transfer image formation.

In accordance with a specifically preferred embodiment of the present invention, a film unit assemblage of the aforementioned general structural parameters will be adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation and may be fabricated to employ, as means interposed intermediate the reception layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment dispersion containing reflecting pigment and at least one optical filter agent, at a pH above the pKa of the optical filter agent and at which pH the dye image-forming material is diffusible during processing as a function of silver halide layer photoexposure, in a concentration in admixture effective to provide a barrier to transmission of actinic radiation therethrough, and the means for interposing the opacifying agent and the processing composition may comprise a rupturable container, retaining the opacifying agent disposed in the processing composition selected, fixedly positioned extending transverse a leading edge of the film unit and adapted, upon application of compressive pressure, to distribute its contents intermediate the reception layer and next adjacent silver halide layer.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a photographic film unit embodying the invention;

FIGS. 2, 4 and 6 are diagrammatic enlarged cross-sectional views of the film unit of FIG. 1, along section line 2—2, illustrating the association of elements during the three illustrated stages of the performance of a diffusion transfer process, for the production of a multicolor transfer image according to the invention, the thickness of the various materials being exaggerated, and wherein FIG. 2 represents an exposure stage, FIG. 4 represents a processing stage and FIG. 6 represents a product of the process; and

FIGS. 3, 5 and 7 are diagrammatic, further enlarged cross-sectional views of the film unit of FIGS. 2, 4 and 6, along section lines 3—3, 5—5 and 7—7, respectively, further illustrating, in detail, the arrangement of layers comprising the photosensitive laminate during the three illustrated stages of the transfer process.

DETAILED DESCRIPTION OF THE INVENTION

As previously characterized, diffusion transfer photographic processing may be employed to provide a positive reflection dye image, as a direct function of actinic radiation incident on a film unit assemblage which unit is preferably constructed to comprise a plurality of sequential layers including a dimensionally stable layer most preferably opaque to incident radiation; a photosensitive silver halide layer having associated therewith dye image-forming material which is processing composition diffusible at a selected first pH as a function of the point-to-point degree of silver halide layer photoexposure; a layer adapted to receive dye image-forming material diffusing thereto; a dimensionally stable layer transparent to incident radiation; means for interposing, intermediate the silver halide layer and the reception layer, opacifying agent and preferably an inorganic reflecting pigment dispersion containing at least one optical filter agent or dye in a concentration effective to provide, subsequent to selective photoexposure of the silver halide layer, protection of the silver halide layer from further exposure to actinic radiation incident on the dimensionally stable layer; and means for converting the pH of the film unit from the first pH to a second pH at which the dye image-forming material is substantially nondiffusible subsequent to substantial dye image-forming material diffusion to the reception layer.

It now has been discovered, however, that a speed increase, in some instances two stops or more, is achieved by effecting development of a film unit which comprises a plurality of layers including a photosensitive layer comprising photosensitive silver halide grains having associated therewith dye image-forming material, preferably a dye developer, in the presence of at least one of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; or the alkyl esters thereof, as an auxiliary developer.

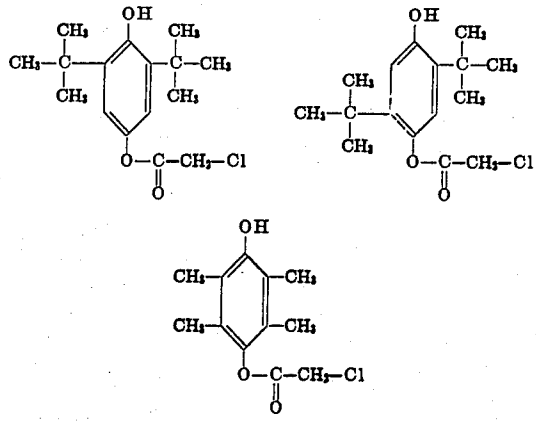
While not intending to be bound by theory, it is believed that the auxiliary developers of the present invention, by giving up one electron, form extremely unreactive semiquinones; i.e., they will not readily reduce silver. The loss of the first electron is relatively rapid. The loss of the second electron results in the formation of a quinone which, as a result of steric hindrance is not subject to nucleophilic attack by other reactants in the system. The first electron which is released immediately results in relatively nondiscriminatory development bringing the exposed grains to a catalytic state which renders them more easily developable by the dye developer. The unexposed grains, while developed to some degree by the auxiliary developer, are not sufficiently reduced to provide measurable interaction with the dye developers.

As with the auxiliary developers set forth in U.S. Pat. No. 2,983,606, the auxiliary developers of the present invention may be contained in the processing composition or in one or more layers of the photosensitive element, e.g., in the silver halide emulsion layer or the layer containing the dye image-forming material. In some instances, it may be desirable to have a portion of the auxiliary developing agent in the processing composition and a portion in the photosensitive element. When the auxiliary developer is contained in the processing composition, it is present at a level of about 0.004–0.008 mg./gm. silver. When employed in the emulsion or adjacent layers the levels are about 0.2 to 5.0 mg./ft.^{2}. The specific amounts employed will vary with a given photographic film unit depending upon the other components of the film unit and the possible interaction between the auxiliary developers and said components.

As stated above, the auxiliary developers may be disposed at various locations in the film unit. However, when the auxiliary developer is disposed in the photosensitive element, certain reagents or components such as sensitizing dyes and the like undergo deleterious reactions with the developer, detracting from the usefulness of the film unit, or even rendering the film unit useless, as by the formation of an excess of fog.

By employing the aforementioned precursor, the auxiliary developer, in an inert form, can be disposed in the film unit in substantially any location, substantially obviating the problem of interferring reactions occurring with other components of the photosensitive element. When the processing composition is applied to the film unit subsequent to exposure, the auxiliary developer is regenerated and able to function as intended.

The preferred precursors are the alkyl esters and the haloalkyl esters, more preferably the monohaloacetate of the specified auxiliary developer. Thus, the preferred precursors are compounds of the formulae:



The alkaline processing composition readily removes the haloacetate group regenerating the hydroxyl to provide the hydroquinone.

The aforementioned preferred precursors are readily prepared by reaction the specific hydroquinone with an alkyl anhydride or a monohaloalkyl anhydride at elevated temperatures.

In a particularly preferred embodiment, it has been found that superior results are obtained if the auxiliary developers of the present invention are employed with

at least a second silver halide developing agent which is not a dye developer. Such developing agents are discussed in detail in U.S. Pat. No. 2,983,606 at column 20, line 40 to column 22, line 44. A particularly preferred developing agent for employment in the present invention comprises 4'-methylphenylhydroquinone.

The following non-limiting example illustrates the preparation of the novel auxiliary developing agent precursor of the present invention.

EXAMPLE

Ten grams each of 2,6-di-t-butyl hydroquinone and monochloroacetic anhydride were mixed and placed in a round bottom flask fitted with a condenser and a drying tube. The mixture was heated with stirring to 80° C. for 5 hours. The resulting oil is cooled and placed into 200 ml. of water and stirred until the oil solidifies. The solid is dissolved in 200 cc. of methanol and precipitated with 300 cc. of water. The precipitate is filtered and washed with water. After drying, the product is recrystallized from hexane to produce the monochloroacetate derivative of 2,6-di-t-butyl hydroquinone melting at 68–69° C. Analysis confirmed the structure.

The silver halide photosensitive layers employed for the fabrication of the photographic film unit, may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water soluble halide, such as ammonium, potassium or sodium chloride, together with corresponding iodide and bromide, in an aqueous solution of a peptizing agent such as colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant dispersion to remove undesirable reaction products and residual water-soluble salts, for example, employing the preferred gelatin matrix material, by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or, alternatively, employing any of the various flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Pat. Nos. 2,614,928; 2,614,929; 2,728,662, and the like; afterripening the dispersion at an elevated temperature in combination with the addition of gelatin or such other polymeric material as may be desired and various adjuncts, for example, chemical sensitizing agents of U.S. Pat. Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., *Photography Its Materials and Processes*, 6th Ed., 1962.

Optical sensitization of the emulsion's silver iodochlorobromide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like; all according to the traditional procedures of the art, as described in Hammer, F. M., *The Cyanine Dyes and Related Compounds.*

Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

As the binder for the photoresponsive material, the aforementioned gelatin may be, in whole or in part, replaced with some natural and/or synthetic processing composition permeable polymeric material such as albumin; casein; or zein or resins such as cellulose derivative, as described in U.S. Pat. Nos. 2,322,085 and 2,541,474; vinyl polymeric such as described in an extensive multiplicity of readily available U.S. and foreign patents or the photoresponsive material may be present substantially free of interstitial binding agent as described in U.S. Pat. Nos. 2,945,771; 3,145,566; 3,142,567; Newman, *Comment on Non-Gelatin Film*, B. J. O. P., 434, Sept. 15, 1961; and Belgian Pat. Nos. 642,557 and 642,558.

As previously mentioned, photosensitive silver iodochlorobromide emulsions possessing the preformed grain size distribution may be readily obtained by a plurality of conventional emulsion manufacturing procedures known to those skilled in the art, including procedures and apparatus particularly adapted to provide restricted and substantially homogeneous or uniform grain size distributions; see, for example, the processes and apparatus disclosed in U.S. Pat. Nos. 3,326,641 and 3,415,650, each of which is specifically hereby incorporated herein by reference.

Reference is now made to FIGS. 1 through 7 of the drawings wherein there is illustrated a preferred film unit of the present invention and wherein like numbers, appearing in the various figures, refer to like components.

As illustrated in the drawings, FIG. 1 sets forth a perspective view of the film unit, designated **10**, and each of FIGS. 2 through 7 illustrate diagrammatic cross-sectional views of film unit **10**, along the stated section lines **2—2, 3—3, 5—5** and **7—7**, during the various depicted stages in the performance of a photographic diffusion transfer process as detailed hereinafter.

Film unit **10** comprises rupturable container **11**, retaining, prior to processing, aqueous processing composition **12**, and photosensitive laminate **13** including, in order, dimensionally stable opaque layer **14**, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer **15**; red-sensitive silver iodochlorobromide emulsion layer **16**; interlayer **17**; magenta dye developer layer **18**; green-sensitive silver iodochlorobromide emulsion layer **19**; interlayer **20**; yellow dye developer layer **21**; blue-sensitive silver iodochlorobromide emulsion layer **22**; auxiliary layer **23**, which may contain an auxiliary silver halide developing agent; image-receiving layer **24**; spacer layer **25**; neutralizing layer **26**; and dimensionally stable transparent layer **27**, preferably an actinic radiation transmissive flexible sheet material.

The structural integrity of laminate **13** may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the laminate at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer **24** and the silver iodochlorobromide emulsion layer next adjacent thereto, for example, image-receiving layer **24** and auxiliary layer **23** as illustrated in FIGS. 2 through 7, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the laminate, in order to facilitate distribution of processing solution **12**

intermediate the stated image-receiving layer **24** and the silver iodochlorobromide emulsion layer next adjacent thereto. The laminate's structural integrity may also be enhanced or provided, in whole or in part, by providing a binding member extending around, for example, the edges of laminate **13**, and maintaining the layers comprising the laminate intact, except at the interface between layers **23** and **24** during distribution of processing composition **12** intermediate those layers. As illustrated in the figures, the binding member may comprise a pressure-sensitive tape **28** securing and/or maintaining the layers of laminate **13** together at its respective edges. Tape **28** will also act to maintain processing solution **12** intermediate image-receiving layer **24** and the silver iodochlorobromide emulsion layer next adjacent thereto, upon application of compressive pressure to pod **11** and distribution of its contents intermediate the stated layers. Under such circumstances, binder tape **28** will act to prevent leakage of fluid processing composition from the film unit's laminate during and subsequent to photographic processing.

Rupturable container **11** may be of the type shown and described in any of U.S. Pat. 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 **29** which are sealed to one another along their longitudinal and end margins to form a cavity in which processing composition **12** is retained. The longitudinal marginal seal **30** is made weaker than the end seals **31** so as to become unsealed in response to the hydraulic pressure generated within the fluid contents **12** of the container by the application of compressive pressure to walls **29** of the container.

As illustrated in FIGS. **1, 2** and **3,** container **11** is fixedly positioned and extends transverse a leading edge of photosensitive laminate **13** whereby to effect unidirectional discharge of the container's contents **12** between image-receiving layer **24** and the stated layer next adjacent thereto, upon application of compressive force to container **11.** Thus, container **11,** as illustrated in FIG. **2,** is fixedly positioned and extends transverse a leading edge of laminate **13** with its longitudinal marginal seal **30** directed toward the interface between image-receiving layer **24** and auxiliary layer **23.** As shown in FIGS. **1, 2** and **4,** container **11** is fixedly secured to laminate **13** by extension **32** of tape **28** extending over a portion of one wall **29** of the container, in combination with a separate retaining member such as illustrated retaining tape **33** extending over a portion of laminate **13**'s surface generally equal in area to about that covered by tape **28.**

As illustrated in FIGS. **1, 2** and **4,** extension flap **32** of tape **28** is preferably of such area and dimensions that upon, for example, manual separation of container **11** and tape **33,** subsequent to distribution of processing composition **12,** from the remainder of film unit **10,** flap **32** may be folded over the edge of laminate **13,** previously covered by tape **33,** in order to facilitate maintenance of the laminate's structural integrity, for example, during the flexations inevitable in storage and use of the processed film unit, and to provide a suitable mask or frame, for viewing of the transfer image through the picture viewing area of transparent layer **27.**

The fluid contents of the container preferably comprise an aqueous alkaline solution having a pH and solvent concentration at which the dye developers are soluble and diffusible and contains inorganic light-reflecting pigment and at least one optical filter agent at a pH above the pKa of such agent in a quantity sufficient, upon distribution, effective to provide a layer exhibiting optical transmission density > about 6.0 and optical reflection density < about 1.0 to prevent exposure of photosensitive silver iodochlorobromide emulsion layers **16, 19** and **22** by actinic radiation incident on dimensionally stable transparent layer **27** during processing in the presence of such radiation and to afford immediate viewing of dye image formation in image-receiving layer **24** during and subsequent to dye transfer image formation. Accordingly, the film unit may be processed, subsequent to distribution of the composition, in the presence of such radiation, in view of the fact that the silver iodochlorobromide emulsion or emulsions of laminate are appropriately protected by incident radiation, at one major surface of the opaque processing composition and at the remaining major surface by the dimensionally stable opaque layer. If the illustrated binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented.

The selected reflecting pigment should be one providing a background suitable for viewing the dye developer transfer image formed in the dyeable polymeric layer. In general, while substantially any reflecting agent may be employed, it is preferred that a reflecting agent be selected that will not interfere with the color integrity of the dye transfer image, as viewed by the observer, and, most preferably, an agent which is aesthetically pleasing to the viewer and does not provide a background noise signal degrading, or detracting from, the information content of the image. Particularly desirable reflecting agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially those agents possessing the optical properties desired for reflection of incident radiation.

As examples of reflecting pigments adapted for employment in the practice of the present invention, mention may be made of barium sulfate, zinc sulfide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

A particularly preferred reflecting agent comprises titanium dioxide due to its highly effective reflection properties. In general, in such preferred embodiment, based upon percent titanium dioxide (weight/volume) a processing composition containing about 1500 to 4000 mgs./ft.^{2} titanium dioxide dispersed in 100 cc. of water will provide a percent reflectance of about 85 to 90 percent. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of > about 85 percent.

In embodiments wherein the dispersion comprises a preformed layer positioned intermediate the reception layer and next adjacent silver iodochlorobromide layer, the pigment layer will be sufficiently transparent to allow transit of exposing radiation through the pigment layer and may comprise titanium dioxide reflecting agent possessing a particle size distribution averaging < about 0.2 μ in diameter and preferably < about 0.05

μ in diameter as initially present preceding exposure of the film unit, which preferred materials, upon contact with aqueous alkaline processing composition, preferably aggregate to provide particles possessing a diameter > about 0.2 μ in diameter and will be coated at a coverage of about 200 to 1000 mgs./ft.^{2}. Specifically, the reflecting agent will be present in a quantity insufficient to prevent exposure of the emulsion layers by actinic radiation incident on the dimensionally stable transparent layer of the film unit but in a concentration sufficient, subsequent to processing, to mask dye developer associated with the silver iodochlorobromide emulsion strata from the dye transfer image. In the preferred construction of such embodiment, the pigment such as titanium dioxide will be initially present in a relatively small particle size to provide unexpectedly efficient transit of radiation through the reflecting layer during exposure which upon contact with an alkaline processing composition and aggregation of the pigment particles provides efficient light reflectivity and masking capacity subsequent to such aggregation.

In general, the reflecting agents to be employed are those which remain substantially immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible inorganic pigment dispersions within the layer in which they are disposed.

Where desired, reflecting agent pigment may thus be distributed in whole or in part within a processing composition permeable polymeric matrix such as gelatin and/or any other such polymeric matrixes as are specifically denoted throughout the specification as suitable for employment as a matrix binder and may be distributed in one or more of the film unit layers which may be separated or contiguous, intermediate the image-receiving layer and next adjacent silver halide layer, provided that its distribution and concentration is effective to provide the denoted post processing masking function, and/or in whole or in part the reflecting agent may be ultimately disposed within the processing composition residuum located intermediate the image-receiving layer and next adjacent silver halide emulsion strata and associated dye image-forming material.

The optical filter agent selected should be one exhibiting, at a pH above its pKa, maximum spectral absorption of radiation at the wavelengths to which the film unit's photosensitive silver halide layer or layers are sensitive and should be substantially immobile or nondiffusible within the pigment dispersion, during performance of its radiation filtration function, in order to maintain and enhance the optical integrity of the dispersion as a radiation filter unit functioning in accordance with the present invention, and to prevent its diffusion into and localized concentration within the image-receiving layer thereby decreasing the efficiency of the reflecting pigment dispersion as a background against which image formation may be immediately viewed, during the initial stages in the diffusion transfer processing of the film unit, by filter agent absorption of dispersion reflected visible radiation prior to reduction in the environmental pH below the pKa of the agent. Commensurate with the spectral sensitivity range of the associated silver halide layer or layers, the optical filter agent selected may comprise one or more filter dyes possessing absorption complementary to such silver iodochlorobromide layers in order to provide effective protection against physical fog providing radiation during processing. Recognizing that the filter agent absorption will derogate from image-viewing characteristics by contaminating reflecting pigment background, the selected agents should be those exhibiting major spectral absorption at the pH at which processing is effected and minimal absorption at a pH below that which obtains during transfer image formation. Accordingly, the selected optical filter agent or agents should possess a pKa below that of the processing pH and above that of the environmental pH subsequent to transfer image formation, and will be preferably selected for employment in the minimum concentration necessary to provide an optical transmission density > about 6.0, at wavelengths at which the silver iodochlorobromide layer is maximally responsive, and an optical reflection density < about 1.0 at such wavelengths.

As specific examples of such pH-sensitive optical filter agents adapted for employment in the practice of the present invention, reference is directed to the agents set forth in aforementioned copending U.S. Pat. application Ser. No. 43,782, filed June 5, 1970, incorporated herein by reference.

In general, preferred agents, both opacifying and filter, are those which remain immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible materials.

As disclosed 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, diethylamine, sodium hydroxide or sodium carbonate 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 disclosed 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, 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 also disclosed to be capable of utilization. As stated, 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 the performance of a diffusion transfer multicolor process employing film unit **10**, the unit is exposed to radiation, actinic to photosensitive laminate **13**, incident on the laminate's exposure surface, as illustrated in FIG. **3**.

Subsequent to exposure, as illustrated by FIGS. **2** and **4**, film unit **10** is processed by being passed through opposed suitably gapped rolls **35** in order to apply compressive pressure to frangible container **11** and to effect rupture of longitudinal seal **30** and distribution of alkaline processing composition **12**, possessing inorganic light-reflecting pigment and optical filter agent at a pH above the pKa of the filter agent and a pH at which the cyan, magenta and yellow dye developers are soluble

and diffusible as a function of the point-to-point degree of exposure of red-sensitive silver iodochlorobromide emulsion layer **16,** green-sensitive silver iodochlorobromide emulsion layer **19** and blue-sensitive silver iodochlorobromide emulsion layer **22,** respectively, intermediate image-receiving layer **24** and auxiliary layer **23.**

Alkaline processing composition **12** permeates emulsion layers **16, 19** and **22** to initiate development of the latent images contained in the respective emulsions. The cyan, magenta and yellow dye developers, of layers **15, 18** and **21,** are immobilized, as a function of the development of their respective associated silver iodochlorobromide emulsions, preferably substantially as a result of their conversion from the reduced form to their relatively insoluble and nondiffusible oxidized form, thereby providing imagewise distributions of mobile, soluble and diffusible cyan, magenta and yellow dye developer, as a function of the point-to-point degree of their associated emulsions' exposure. At least part of the imagewise distributions of mobile cyan, magenta and yellow dye developer transfers, by diffusion, to dyeable polymeric layer **24** to provide a multicolor dye transfer image to that layer which is viewable against the background provided by the reflecting pigment present in processing composition residuum **12** masking cyan, magenta and yellow dye developer remaining associated with blue-sensitive emulsion layer **22,** green-sensitive emulsion layer **19** and red-sensitive emulsion layer **16.** Subsequent to substantial transfer image formation, a sufficient portion of the ions comprising aqueous alkaline processing composition **12** transfer, by diffusion, through permeable polymeric reception layer **24,** permeable spacer layer **25** to polymeric neutralizing layer **26** whereby the environmental pH of the system decreases as a function of neutralization to a pH at which the cyan, magenta and yellow dye developers, in the reduced form, are substantially nondiffusible to thereby provide a stable multicolor dye transfer image and discharge of the pH-sensitive optical filter agent by reduction of the pH substantially below the pKa of such agent to thereby provide maximum reflectivity in terms of the pigment concentration present.

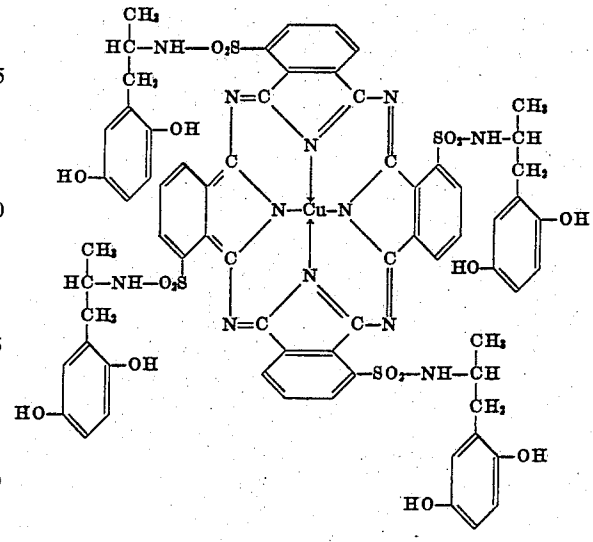
The alkaline solution component of the processing composition, positioned intermediate the photosensitive element and the image-receiving layer, thus permeates the emulsions to initiate development of the latent images contained therein. The respective associated dye developers are mobilized in unexposed areas as a consequence of the development of the latent images. This mobilization is apparently, at least in part, due to a change in the solubility characteristics of dye developer upon oxidation and especially as regards its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent, and in part to a localized exhaustion of alkali as a result of development. In unexposed and partially exposed areas of the emulsions, the associated dye developer is diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver iodochlorobromide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, said transfer substantially excluding oxidized dye developer. The image-receiving element receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide the reversed or positive color image of the developed image.

Subsequent to distribution of processing composition **12,** container **11** may be manually dissociated from the remainder of the film unit, as described above, to provide the product illustrated in FIG. **6.**

The present invention will be further illustrated and detailed in conjunction with the following illustrative constructions which set out representative embodiments and photographic utilization of the novel photographic film units of this invention, which, however, are not limited to the details therein set forth and are intended to be illustrative only.

Film units similar to those shown in the drawings may be prepared, for example, by coating, in succession, on a 5 mil. opaque polyester film base, the following layers:

1. a layer of the cyan dye developer

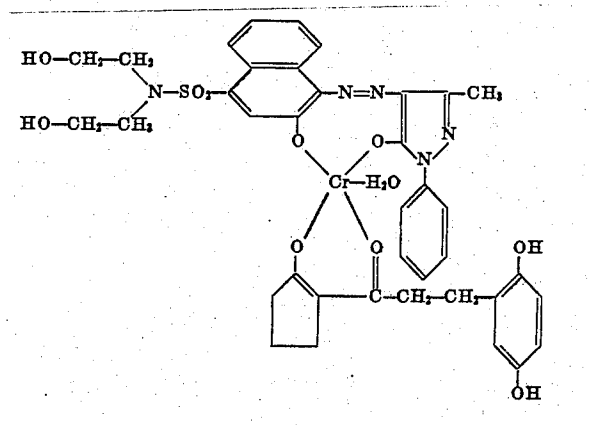


dispersed in gelatin and coated at a coverage of about 100 mgs./ft.^{2} of dye and about 130 mgs./ft.^{2} of gelatin;

2. a red-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 140 mgs./ft.^{2} of silver and about 62 mgs./ft.^{2} of gelatin;

3. a layer of butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of about 32:1, respectively, at a coverage of about 140 mgs./ft.^{2};

4. a layer of the magenta dye developer

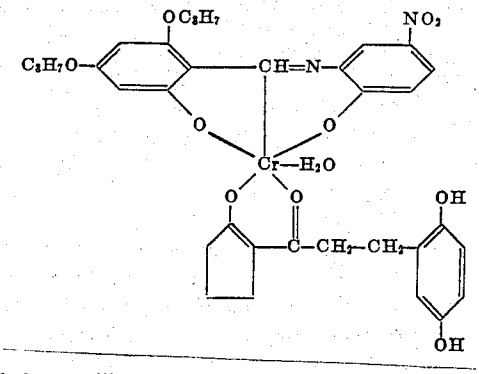


dispersed in gelatin and coated at a coverage of about 110 mgs./ft.^{2} of dye and about 100 mgs./ft.^{2} of gelatin;

5. a green-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 100 mgs./ft.^{2} of silver and 44 mgs./ft.^{2} of gelatin;

6. a layer comprising butyl acrylate/diacetone acrylamide/styrene/methacrylic acid (60/30/4/6) and polyacrylamide coated in a ratio of about 7:1, respectively, at a coverage of about 107 mgs./ft.^{2};

7. a layer of the yellow dye developer



and the auxiliary developer 4'-methylphenylhydroquinone dispersed in gelatin and coated at a coverage of about 70 mgs./ft.^{2} of dye and 54 mgs./ft.^{2} of gelatin;

8. a blue-sensitive gelatino-silver iodochlorobromide emulsion coated at a coverage of about 120 mgs./ft.^{2} of silver, about 75 mgs./ft.^{2} of gelatin, and 30 mgs./ft.^{2} of auxiliary developer; and

9. a layer of gelatin coated at a level of about 40 mgs./ft.^{2}.

Then a transparent 5 mil. polyester film base may be coated, in succession, with the following illustrative layers:

1. a 7:3 mixture, by weight, of polyethylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1400 mgs./ft.^{2}, to provide a polymeric acid layer;

2. a copolymer of n-butyl acrylate, styrene, methacrylic acid and diacetone acrylamide in a weight ratio of 60:4:6:30 at a coverage of about 500 mgs./ft.^{2}, to provide a polymeric spacer layer; and

3. a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of about 400 mgs./ft.^{2} and including about 20 mgs./ft.^{2} of 1-phenyl-5-mercaptotetrazole, to provide a polymeric image-receiving layer.

The two components thus prepared may then be taped together in laminate form, at their respective edges, by means of a pressure-sensitive binding tape extending around, in contact with, and over the edges of the resultant laminate.

A rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising:

Water	100.0 cc.
Potassium hydroxide	7.5 gms.
Carboxymethyl cellulose sodium salt	3.40 gms.
N-phenethyl-α-picolinium bromide	1.72 gms.
Cesium hydroxide	4.7 gms.
Benzotriazole	1.0 gms.
6-bromo-5-methyl-4-azabenzimidazole	0.05 gms.
Titanium dioxide	50.0 gms.
2-methylimidazole	0.35 gms.

may then be fixedly mounted on the leading edge of each of the laminates, by pressure-sensitive tapes interconnecting the respective containers and laminates, such that, upon application of compressive pressure to a container, its contents may be distributed, upon rupture of the container's marginal seal, between the polymeric image-receiving layer and next adjacent layer.

The auxiliary developer of the present invention may be disposed in one or more of the above emulsion layers, dey developer layers or in the processing solution at levels previously designated.

The photosensitive composite film units may be exposed to radiation incident on the transparent polyester layer through a conventional step wedge and processed by passage of the exposed film units through appropriate pressure-applying members, such as suitably gapped, opposed rolls, to effect rupture of the container and distribution of its contents. Subsequent to processing, the multicolor dye transfer image formation may be viewed through the transparent polyester layer against the titanium dioxide background provided by distribution of the pigment containing processing composition between layer **9** and the polymeric image-receiving layer.

The following non-limiting examples illustrate the employment of the auxiliary developers of the present invention in monochromatic film units.

2,6-di-t-butyl hydroquinone was tested at various levels in monochrome film units and processed as described above.

EXAMPLE II

A 5 mil. opaque polyester film support was coated, in order, with 50 mgs./ft.^{2} of the above-indicated magenta dye developer dispersed in 750 mgs./ft.^{2} of gelatin and 7.5 mgs./ft.^{2} of 4'-methylphenylhydroquinone; a green-sensitive gelatin-silver iodochlorobromide emulsion coated at a level of about 150 mgs./ft.^{2} of silver and 150 mgs./ft.^{2} of gelatin; and a gelatin layer coated at a level of about 30 mgs./ft.^{2}. 2,6-di-t-butyl hydroquinone was disposed in the emulsion layer as a solid dispersion. The film unit was exposed and processed and the relative speed determined from an H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone	0	0.30	0.60
Relative speed	100	177	196

From the foregoing it will be noted that a speed increase of almost 3 stops can be achieved over the control by the auxiliary developer of the present invention. However, it is also noted that with the given system, an excessive amount of 2,6-di-t-butyl hydroquinone can lead to fog.

EXAMPLE III

A film unit was prepared by coating a 5 mil. opaque polyester film base with 50 mgs./ft.^{2} of the above-

indicated yellow dye developer dispersed in gelatin at a level of about 50 mgs./ft.^{2} of dye and about 75 mgs./ft.^{2} of gelatin, a blue-sensitive gelatin-silver iodochlorobromide emulsion coated at a coverage of about 150 mgs./ft.^{2} of silver and about 150 mgs./ft.^{2} of gelatin, and 7.5 mgs./ft.^{2} of 4'-methylphenylhydroquinone; and a gelatin layer coated at a level of 30 mgs./ft.^{2} of 2,6-di-t-butyl hydroquinone was disposed in the emulsion layer at various levels as a solid dispersion. The film unit was exposed and processed and the speed determined from and H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone	0	0.30	0.60
Relative speed	100	120	147

EXAMPLE IV

A 5 mil. opaque polyester support was coated with 50 mgs./ft.^{2} of the cyan dye developer indicated above and 75 mgs./ft.^{2} of gelatin; a red-sensitive gelatin-silver iodochlorobromide emulsion coated at a level of about 150 mgs./ft.^{2} of silver and 150 mgs./ft.^{2} of gelatin; and a layer of gelatin coated at 30 mgs./ft.^{2}. 2,6-di-t-butyl hydroquinone was disposed in the emulsion layer as a solid dispersion. The film unit was exposed and processed and the speed determined on an H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone	0	0.30	0.60
Relative speed	100	113	124

EXAMPLE V

A 5 mil. opaque polyester film support was coated, in order, with 65 mgs./ft.^{2} of the above-indicated magenta dye developer dispersed in 50 mgs./ft.^{2} of gelatin and 7.5 mgs./ft.^{2} 4'-methylphenylhydroquinone; a green-sensitive gelatin-silver iodochlorobromide emulsion coated at a level of about 80 mgs./ft.^{2} of silver and 40 mgs./ft.^{2} of gelatin; and a gelatin layer coated at a level of about 30 mgs./ft.^{2}. The 2,6-di-t-butyl hydroquinone chloroacetate ester was dispersed in the emulsion layer as an oil dispersion. The film unit was exposed and processed and the speed determined from an H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone chloroacetate ester	0	0.64	7.28	1.92	2.56	3.20
Relative speed	100	114	100	127	136	142

EXAMPLE VI

A film unit was prepared by coating a 5 mil. opaque polyester film base with 70 mgs./ft.^{2} of the above-indicated yellow dye developer dispersed in gelatin at a level of about 70 mgs./ft.^{2} of dye and about 70 mgs./ft.^{2} of gelatin, a blue-sensitive gelatin-silver iodochlorobromide emulsion coated at a coverage of about 65 mgs./ft.^{2} of silver and about 50 mgs./ft.^{2} of gelatin and 7.5 mgs./ft.^{2} of 4'-methylphenylhydroquinone; and a gelatin layer coated at a level of 30 mgs./ft.^{2} of 2,6-di-t-butyl hydroquinone chloroacetate ester was disposed in the emulsion layer at various levels as an oil dispersion. The film unit was exposed and processed and the speed determined from and H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone chloroacetate ester	0	0.64	1.28	1.92	2.56	3.20
Relative speed	100	105	114	122	124	126

EXAMPLE VII

A 5 mil. opaque polyester support was coated with 100 mgs./ft.^{2} of the cyan dye developer indicated above and 92 mgs./ft.^{2} of gelatin; a red-sensitive gelatin-silver iodochlorobromide emulsion coated at a level of about 140 mgs./ft.^{2} of silver and 27 mgs./ft.^{2} of gelatin; and a layer of gelatin coated at 30 mgs./ft.^{2}. The 2,6-di-t-butyl hydroquinone chloroacetate ester was disposed in the emulsion layer as an oil dispersion. The film unit was exposed and processed and the speed determined on an H & D curve.

CONTROL

mgs./ft.^{2} 2,6-di-t-butyl hydroquinone chloroacetate ester	0	1.28	1.92	2.56
Relative speed	100	108	118	127

From the foregoing it will be noted that a speed increase is noted at various levels with both the auxiliary developer per se and with the precursor of the developer. Similar results may be achieved with 2,5-di-t-butyl hydroquinone, durohydroquinone and their precursors.

The pH and solvent concentration of the alkaline processing solution initially employed will possess a pH above the pKa of the optical filter agents where the latter are employed, that is, the pH at which about 50 percent of the agents are present as the lesser absorbing species and about 50 percent are present as the greater absorbing species, preferably, a pKa of > about 11 and most preferably > about 12 and a pH at which the dye developers employed are soluble and diffusible. Although it has been found that the specific pH to be employed may be readily determined empirically for any dye developer and optical filter agent, or group of dye developers and filter agents, most particularly desirable

dye developers are soluble at pH's above 9 and relatively insoluble at pH's below 9, in reduced form, and relatively insoluble at substantially any alkaline pH, in oxidized form, and the system can be readily balanced accordingly for such dye developers. In addition, although as previously noted, the processing composition, in the preferred embodiment, will include the stated film-forming viscosity-increasing agent, or agents, to facilitate spreading of the composition and to provide maintenance of the spread composition as a structurally stable layer of the laminate, subsequent to distribution, it is not necessary that such agent be employed as a component of the composition.

Neutralizing means, for example, a polymeric acid layer of the type discussed above may be incorporated, as stated, in the film unit of the present invention, to provide reduction of the alkalinity of the processing solution from a pH above the pKa of the optical filter agent selected at which the dyes are soluble to a pH below the pKa of the agent at which the dyes are substantially nondiffusible, in order to advantageously further stabilize and optimize reflectivity of the dye transfer image. In such instance, the neutralizing layer may comprise particulate acid reacting reagent dispersed within the film unit or a polymer acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mils. in thickness, positioned intermediate the transparent support and image-receiving layer, and/or the opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer, for example, approximating 0.1 to 0.7 mil. in thickness, next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

Specifically, the film units may employ the presence of a polymeric acid layer such as, for example, of the type set forth in U.S. Pat. No. 3,362,819 which, most preferably, includes the presence of an inert timing or spacer layer intermediate the polymeric acid layer carried on a support and the image-receiving layer.

As set forth in the last-mentioned patent, the polymeric acid layer may comprise polymers which contain acid groups, such as carboxylic acid and sulfonic acid groups, which are capable of forming salts with alkali metals, such as sodium, potassium etc., or with organic bases, particularly quaternary ammonium bases, such as tetramethyl ammonium hydroxide, or potentially acid-yielding groups, such as anhydrides or lactones, or other groups which are capable of reacting with bases to capture and retain them. The acid-reacting group is, of course, retained in the polymer layer. In the preferred embodiments disclosed, the polymer contains free carboxy groups and the transfer processing composition employed contains a large concentration of sodium and/or potassium ions. The acid polymers stated to be most useful are characterized by containing free carboxyl groups, being insoluble in water in the free acid form, and by forming water-soluble sodium and/or potassium salts. One may also employ polymers containing carboxylic acid anhydride groups, at least some of which preferably have been converted to free carboxyl groups prior to imbibition. While the most readily available polymeric acids are derivatives of cellulose or of vinyl polymers, polymeric acids from other classes of polymers may be used. As examples of specific polymeric acids set forth in the application, mention may be made of dibasic acid half-ester derivatives of cellulose which derivatives contain free carboxyl groups, e.g., cellulose acetate hydrogen phthalate, cellulose acetate hydrogen glutarate, cellulose acetate hydrogen succinate, ethyl cellulose hydrogen succinate, ethyl cellulose acetate hydrogen succinate, cellulose acetate hydrogen succinate hydrogen phthalate; ether and ester derivatives or cellulose modified with sulfoanhydrides, e.g., with ortho-sulfobenzoic anhydride; polystyrene sulfonic acid; carboxymethyl cellulose; polyvinyl hydrogen phthalate; polyvinyl acetate hydrogen phthalate; polyacrylic acid, acetals of polyvinyl alcohol with carboxy or sulfo substituted aldehydes, e.g., o-, m-, or p-benzaldehyde sulfonic acid or carboxylic acid; partial esters of ethylene/maleic anhydride copolymers; partial esters of methyl-vinyl ether/maleic anhydride copolymers; etc.

As previously noted, the pH of the processing composition preferably is of the order of at least 12 to 14 and the pKa of the selected optical filter agents will accordingly preferably be in the order of 13 or greater. The polymer layer is disclosed to contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 12 to 14 to a pH of at least 11 or lower at the end of the imbibition period, and preferably to a pH of about 5 to 8 within a short time after imbibition, thus requiring, of course, that the action of the polymeric acid be accurately so controlled as not to interfere with either development of the negative or image transfer of unoxidized dye developers. For this reason, the pH of the image layer must be kept at a functional transfer level, for example, 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to a pH below that at which dye transfer may be accomplished, for example, at least about 11 and preferably about pH 9 to 10. Unoxidized dye developers containing hydroquinonyl developing radicals diffuse from the negative to the positive as the sodium or other alkali salt. The diffusion rate of such dye image-forming components thus is at least partly a function of the alkali concentration, and it is necessary that the pH of the image layer remain on the order of, for example, 12 to 14 until transfer of the necessary quantity of dye has been accomplished. The subsequent pH reduction, in addition to its desirable effect upon image light stability, serves a highly valuable photographic function by substantially terminating further dye transfer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, by an undesired reduction in positive image density, the acid groups are disclosed to be so distributed in the polymer layer that the rate of their availability to the alkali is controllable, e.g., as a function of the rate of swelling of the polymer layer which rate in turn has a direct relationship to the diffusion rate of the alkali ions. The desired distribution of the acid groups in the polymer may be effected by mixing acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only an acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited copending application, by (a) a mixture of cellulose acetate and cellulose acetate hydrogen phthalate and (b) a cellulose acetate hydrogen phthalate polymer having a much lower percentage of phthayl groups than the first-mentioned cellulose acetate hydrogen phthalate.

It is also there disclosed that the layer containing the polymeric acid may contain a water-insoluble polymer, preferably a cellulose ester, which acts to control or modulate the rate at which the alkali salt of the polymer acid is formed. As examples of cellulose esters contemplated for use, mention is made of cellulose acetate, cellulose acetate butyrate, etc. The particular polymers and combinations of polymers employed in any given embodiment are, of course, selected so as to have adequate wet and dry strength and when necessary or desirable, suitable subcoats are employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer of the last-mentioned patent, for example, an inert spacer layer comprising polyvinyl alcohol or gelatin, acts to "time" control the pH reduction by the polymeric acid layer. This timing is disclosed to be a function of the rate at which the alkali diffuses through the inert spacer layer. It is there stated to have been found that the pH does not drop until the alkali has passed through the spacer layer, i.e., the pH is not reduced to any significant extent by the mere diffusion into the interlayer, but the pH drops quite rapidly once the alkali diffuses through the spacer layer.

As disclosed in aforementioned U.S. Pat. No. 3,362,819, the presence of an inert spacer layer was found to be effective in evening out the various reaction rates over a wide range of temperatures, for example, by preventing premature pH reduction when imbibition is effected at temperatures above room temperature, for example, at 95 to 100° F. By providing an inert spacer layer, that application discloses that the rate at which alkali is available for capture in the polymeric acid layer becomes a function of the alkali diffusion rates.

However, as disclosed in U.S. Pat. No. 3,455,686 preferably the aforementioned rate at which the cations of the alkaline processing composition, i.e., alkali ions, are available for capture in the polymeric acid layer should be decreased with increasing transfer processing temperatures in order to provide diffusion transfer color processes relatively independent of positive transfer image variations over an extended range of ambient temperatures.

Specifically, it is there stated to have been found that the diffusion rate of alkali through a permeable inert polymeric spacer layer increases with increased processing temperature to the extent, for example, that at relatively high transfer processing temperatures, that is, transfer processing temperatures above approximately 80° F., a premature decrease in the pH of the transfer processing composition occurs due, at least in part, to the rapid diffusion of alkali from the dye transfer environment and its subsequent neutralization upon contact with the polymeric acid layer. This was stated to be especially true of alkali traversing an inert spacer layer possessing permeability to alkali optimized to be effective with the temperature range of optimum transfer processing. Conversely, at temperatures below the optimum transfer processing range, for example, temperatures below approximately 40° F., the last-mentioned inert spacer layer was disclosed to provide an effective diffusion barrier timewise preventing effective traverse of the inert spacer layer by alkali having temperature depressed diffusion rates and to result in maintenance of the transfer processing environment's high pH for such an extended time interval as to facilitate formation of transfer image stain and its resultant degradation of the positive transfer images' color definition.

It is further stated in the last-mentioned U.S. Pat. No. 3,455,686 to have been found, however, that if the inert spacer layer of the print-receiving element is replaced by a spacer layer which comprises a permeable polymeric layer exhibiting permeability inversely dependent on temperature, that is, a polymeric film-forming material which exhibits decreasing permeability to solubilized alkali derived cations such as alkali metal and quaternary ammonium ions under conditions of increasing temperature, that the positive transfer image defects resultant from the aforementioned overextended pH maintenance and/or premature pH reduction are obviated.

As examples of polymers which were disclosed to exhibit inverse temperature-dependent permeability to alkali, mention may be made of: hydroxypropyl polyvinyl alcohol, polyvinyl methyl ether, polyethylene oxide, polyvinyl oxazolidone, hydroxypropyl methyl cellulose, isopropyl cellulose, partial acetals of polyvinyl alcohol such as partial polyvinyl butyral, partial polyvinyl formal, partial polyvinyl acetal, partial polyvinyl propional, and the like.

The last-mentioned specified acetals of polyvinyl were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1000, preferably of about 1000 to 50,000, possessing a degree of acetalation within about 10 to 30 percent, 10 to 30 percent, 20 to 80 percent, and 10 to 40 percent, of the polyvinyl alcohol's theoretical polymeric hydroxy groups, respectively, and including mixed acetals where desired.

Where desired, a mixture of the polymers may be employed, for example, a mixture of hydroxypropyl methyl cellulose and partial polyvinyl butyral.

Employment of the detailed and preferred film units of the present invention, according to the herein described color diffusion transfer process, specifically provides for the production of a highly stable transfer image accomplished, at least in part, by effectively obviating the previously discussed disadvantages of the prior art products and processes, by in process adjustment of the environmental processing composition solvent and pH concentration from a solvent and pH concentration at which dye diffusion or transfer is operative to a solvent and pH concentration at which dye transfer is inoperative subsequent to substantial transfer image formation. The stable color transfer image is obtained irrespective of the fact that the film unit is maintained as an integral laminate unit during exposure, processing, viewing, and storage of the unit. Accordingly, by means of the present invention, multicolor transfer images may be provided over an extended processing temperature range which exhibit desired maximum and minimum dye transfer image densities; yellow, magenta and cyan dye saturation; red, green and blue hues; and color separation. These unexpected advantages are in addition to the manufacturing advantages obtained by reason of the present invention's integral color transfer film unit construction and which will be readily apparent from examination of the unit's parameters, that is, for example, advantages in more efficient utilization of fabricating materials and components, enhanced simplicity of film manufacture and camera design and construction, and more simplified and effectively controlled customer utilization of the unit.

The dimensionally stable support layers referred to may comprise any of the various types of conventional opaque and transparent rigid or flexible materials possessing the requisite liquid impermeability and, preferably, the vapor transmissivity denoted above, may comprise polymeric films of both synthetic types and those derived from naturally occurring products. Particularly suitable materials include aqueous alkaline solution impermeable, water vapor permeable, flexible polymeric materials such as vapor permeable polymeric films derived from ethylene glycol terephthalic acid, vinyl chloride polymers; polyvinyl acetate; polyamides; polymethacrylic acid methyl and ethyl esters; cellulose derivatives such as cellulose, acetate, triacetate, nitrate, propionate, butyrate, acetate-propionate, or acetate-butyrate; alkaline solution impermeable, water vapor permeable papers; crosslinked polyvinyl alcohol; regenerated cellulose; and the like.

As examples of materials, for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylon as, for example, N-methoxymethyl polyhexamethylene adipamide; partially hydrolyzed polyvinyl acetate; polyvinyl alcohol with or without plasticizers; cellulose acetate with filler as, for example, one-half cellulose acetate and one-half oleic acid; gelatin; and other materials of a similar nature. 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.

In addition, development may be effected in the presence of an onium compound, particularly a quaternary ammonium compound, in accordance with the processes disclosed in U.S. Pat. No. 3,173,786, issued Mar. 16, 1965.

It will be apparent that the relative proportions of the agents of the diffusion transfer processing composition may be altered to suit the requirements of the operator. Thus, it is within the scope of this invention to modify the herein described developing compositions by the substitution of preservatives, alkalies, etc., other than those specifically mentioned, provided that the pH of the composition is initially at the first pH and solvent concentration required. When desirable, it is also contemplated to include, in the developing composition, components such as restrainers, accelerators, etc. Similarly, the concentration of various components may be varied over a wide range and when desirable adaptable components may be disposed in the photosensitive element, prior to exposure, in a separate permeable layer of the photo-sensitive element and/or in the photosensitive emulsion.

In all examples of this specification, percentages of components are given by weight unless otherwise indicated.

An extensive compilation of specific dye developers particularly adapted for employment in photograhpic diffusion transfer processes is set forth in 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 process use, mention may also be made of U.S. Pat. Nos. 2,983,605; 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.

As additional examples of synthetic, film-forming, permeable polymers particularly adapted to retain dispersed dye developer, mention may be made of nitrocarboxymethyl cellulose, as disclosed in U.S. Pat. No. 2,992,104; an acylamidobenzene sulfo ester of a partial sulfobenzal of polyvinyl alcohol, as disclosed in U.S. Pat. No. 3,043,692; polymers of N-alkyl-α, β-unsaturated carboxamides and copolymers of N-alkyl-α,β-carboxamides with N-hydroxyalkyl-α,β-unsaturated carboxamides, as disclosed in U.S. Pat. No. 3,069,263; copolymers of vinylphthalimide and α, β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,061,428; copolymers of N-vinylpyrrolidones and α,β-unsaturated carboxylic acids and terpolymers of N-vinylpyrrolidones, α, β-unsaturated carboxylic acids and alkyl esters of α, βunsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,044,873; copolymers of N,N-dialkyl-α,β-unsaturated carboxamides with α,β-unsaturated carboxylic acids, the corresponding amides of such acids, and copolymers of N-aryl- and N-cycloalkyl-α,β-unsaturated carboxamides with α, β-unsaturated carboxylic acids, as disclosed in U.S. Pat. No. 3,069,296; and the like.

In addition to conventional techniques for the direct dispersion of a particulate solid material in a polymeric, or colloidal, matrix such as ball-milling and the like techniques, the preparation of the dye developer dispersion may also be obtained by dissolving the dye in an appropriate solvent, or mixture of solvents, and the resultant solution distributed in the polymeric binder, with optional subsequent removal of the solvent, or solvents, employed, as, for example, by vaporization where the selected solvent, or solvents, possesses a sufficiently low boiling point or washing where the selected solvent, or solvents, possesses a sufficiently high differential solubility in the wash medium, for example, water, when measured against the solubility of the remaining composition components, and/or obtained by dissolving both the polymeric binder and dye in a common solvent.

For further detailed treatment of solvent distribution systems of the types referred to above, and for an extensive compilation of the conventional solvents traditionally employed in the art to effect distribution of photographic color-providing materials in polymeric binders, specifically for the formation component layers of photographic film units, reference may be made to U.S. Pat. Nos. 2,269,158; 2,322,027; 2,304,939; 2,304,940; 2,801,171; and the like.

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. Pat. 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, react-

ing 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 imagewise 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.

Although the preceding description of the invention has been couched in terms of the preferred photosensitive component construction wherein at least two selectively sensitized photosensitive strata are in contiguous coplanar relationship and, specifically, in terms of the preferred tripack type structure comprising a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum having associated therewith, respectively a cyan dye developer, a magenta dye developer and a yellow dye developer, the photosensitive component of the film unit may comprise at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen wherein each of the minute photosensitive elements has associated therewith, for example, an appropriate dye developer in or behind its respective silver halide emulsion portion. In general, a suitable photosensitive screen will comprise minute red-sensitized emulsion elements, minute green-sensitized emulsion elements and minute blue-sensitized emulsion elements arranged in side-by-side relationship in a screen pattern and having associated therewith, respectively, a cyan, a magenta and a yellow dye developer.

The present invention also includes the employment of a black dye developer and the use of a mixture of dye developers adapted to provide a black-and-white transfer image, for example, the employment of dye developers of the three subtractive colors in an appropriate mixture in which the quantities of the dye developers are proportioned such that the colors combine to provide black.

Where in the specification, 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 transparencey. 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.

It will be recognized that, by reason of the preferred film unit's structural parameters, the transfer image formed upon directed exposure of the film unit to a selected subject and processing, will be a geometrically reversed image of the subject. Accordingly, to provide transfer image formation geometrically nonreversed, exposure of such film unit should be accomplished through an image-reversing optical system such a camera possessing an image-reversing optical system.

In addition to the described essential layers, it will be recognized that the film unit may also contain one or more subcoats or layers, which, in turn, may contain one or more additives such as plasticizers, intermediate essential layers for the purpose, for example, of improving adhesion, and that any one or more of the described layers may comprise a composite of two or more strata of the same, or different, components and which may be contiguous, or separated from, each other, for example, two or more neutralizing layers or the like, one of which may be disposed intermediate the cyan dye image-forming component retaining layer and the dimensionally stable opaque 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 film unit comprising photosensitive silver halide and an auxiliary silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the alkyl and haloalkyl ester precursors thereof wherein said silver halide layer has additionally associated therewith a dye which has a dihydroxyphenyl silver halide developing function.

2. A product as defined in claim **1** wherein said film unit comprises a support carrying a photosensitive silver halide layer having associated therewith said auxiliary developing agent and said dye.

3. A product as defined in claim **2** wherein said auxiliary developing agent is disposed in a layer adjacent said silver halide layer.

4. A product as defined in claim **2** wherein said auxiliary developing agent is disposed in said silver halide layer.

5. A product as defined in claim **1** wherein said haloalkyl ester is the monochloroacetate ester.

6. A product as defined in claim **1** which includes as a second auxiliary developing agent a hydroquinone silver halide developing agent which is substantially colorless at least in its unoxidized form.

7. A product as defined in claim **6** wherein said hydroquinone silver halide developing agent is 4-methylphenyl hydroquinone.

8. A product as defined in claim **1** which comprises a plurality of layers including a support layer carrying on one surface, in order, a silver halide emulsion layer having associated therewith a diffusion transfer process dye image-forming material which has a dihydroxyphenyl silver halide developing function; an auxiliary silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the alkyl and haloalkyl ester precursors thereof; reflecting means adapted to mask dye image-forming material associated with said silver halide emulsion layer subsequent to processing of the film unit; and a polymeric layer dyeable by said dye image-forming material.

9. A product as defined in claim 8 which is adapted to be processed by passing said member between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive element including a composite structure containing as essential layers, in sequence, a first dimensionally stable layer opaque to incident actinic radiation, a photosensitive silver halide emulsion layer having associated therewith a diffusion transfer process dye image-forming material which has a dihydroxy-phenyl silver halide developing function, and means securing said layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing composition containing reflecting agent fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent thereto upon application of compressive force to said container; and

an auxiliary silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the alkyl and haloalkyl ester precursors thereof.

10. A product as defined in claim 9 wherein said auxiliary silver halide developing agent is disposed in said silver halide emulsion layer.

11. A product as defined in claim 10 wherein said auxiliary silver halide developing agent is disposed as the haloalkyl ester precursor.

12. A product as defined in claim 9 wherein said auxiliary silver halide developing agent is disposed in said rupturable container.

13. A product as defined in claim 9 wherein said reflecting agent is titanium dioxide.

14. A product as defined in claim 9 including at least one acid reacting polymeric layer positioned intermediate at least one of said first dimensionally stable opaque layers and the photosensitive silver halide emulsion layer next adjacent thereto, and said dimensionally stable transparent layer and the dyeable polymeric layer next adjacent thereto and said processing composition comprises an aqueous alkaline processing composition.

15. A product as defined in claim 14 wherein said polymeric acid layer contains sufficient acidifying function to effect reduction of said processing composition from a first pH at which said dye image-forming material is substantially soluble and diffusible to a second pH at which said image-forming material is substantially nondiffusible.

16. A product as defined in claim 15 wherein said photosensitive element includes at least two selectively sensitized silver halide emulsion layers, each having a dye of predetermined color associated therewith, which has a dihydroxyphenyl silver halide developing function, each of said dyes soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsion associated therewith at said first pH and substantially non-diffusible in said alkaline processing composition at said second pH.

17. A process for forming photographic images which includes, in combination, the steps of exposing a photosensitive element comprising a plurality of layers including a support carrying on one surface a photosensitive silver halide layer, said silver halide layer having a dye associated therewith, which has a dihydroxyphenyl silver halide developing function; contacting said photosensitive layer with an aqueous alkaline processing composition and an auxiliary silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the alkyl and haloalkyl ester precursors thereof for a time sufficient to develop a latent image in said photosensitive silver halide layer to a visible image.

18. A process as defined in claim 17 wherein said auxiliary developing agent is initially disposed in said aqueous alkaline processing composition.

19. A process as defined in claim 17 wherein said auxiliary developing agent is initially associated with said photosensitive element.

20. A process as defined in claim 19 wherein said auxiliary developing agent is initially disposed in said silver halide layer.

21. A process as defined in claim 20 wherein said auxiliary silver halide developing agent is initially disposed in said silver halide layer as said precursor.

22. A process as defined in claim 17 which comprises, in combination, the steps of:

a. exposing a photographic film unit which comprises a plurality of layers including a photosensitive silver halide layer having associated therewith a diffusion transfer process dye image-providing material which has a dihydroxyphenyl silver halide developing function and a diffusion transfer process image-receiving layer adapted to receive solubilized image-forming material diffusing thereto;

b. contacting said photosensitive silver halide emulsion with an aqueous alkaline processing composition and an auxiliary silver halide developing agent selected from the group consisting of 2,6-di-t-butyl hydroquinone; 2,5-di-t-butyl hydroquinone; durohydroquinone; and the alkyl and haloalkyl ester precursors thereof;

c. effecting thereby substantial development of said silver halide emulsion;

d. forming thereby an imagewise distribution of mobile image-forming material as a function of the point-to-point degree of emulsion exposure; and

e. transferring by diffusion at least a portion of said imagewise distribution of mobile image-forming material to said layer adapted to receive said material to provide thereto an image in terms of said imagewise distribution.

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