

[54] PHOTOGRAPHIC PRODUCTS,
PROCESSES AND COMPOSITIONS

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[73] Assignee: Polaroid Corporation, Cambridge, Mass.
[22] Filed: Dec. 28, 1970
[21] Appl. No.: 101,968

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 786,352, Dec. 23, 1968, Continuation-in-part of Ser. No. 43,782, June 5, 1970, abandoned.
[52] U.S. Cl. 96/3, 96/29 D, 96/84 R
[51] Int. Cl. G03c 5/54, G03c 7/00, G03c 1/84
[58] Field of Search 96/3, 29 D, 84 R

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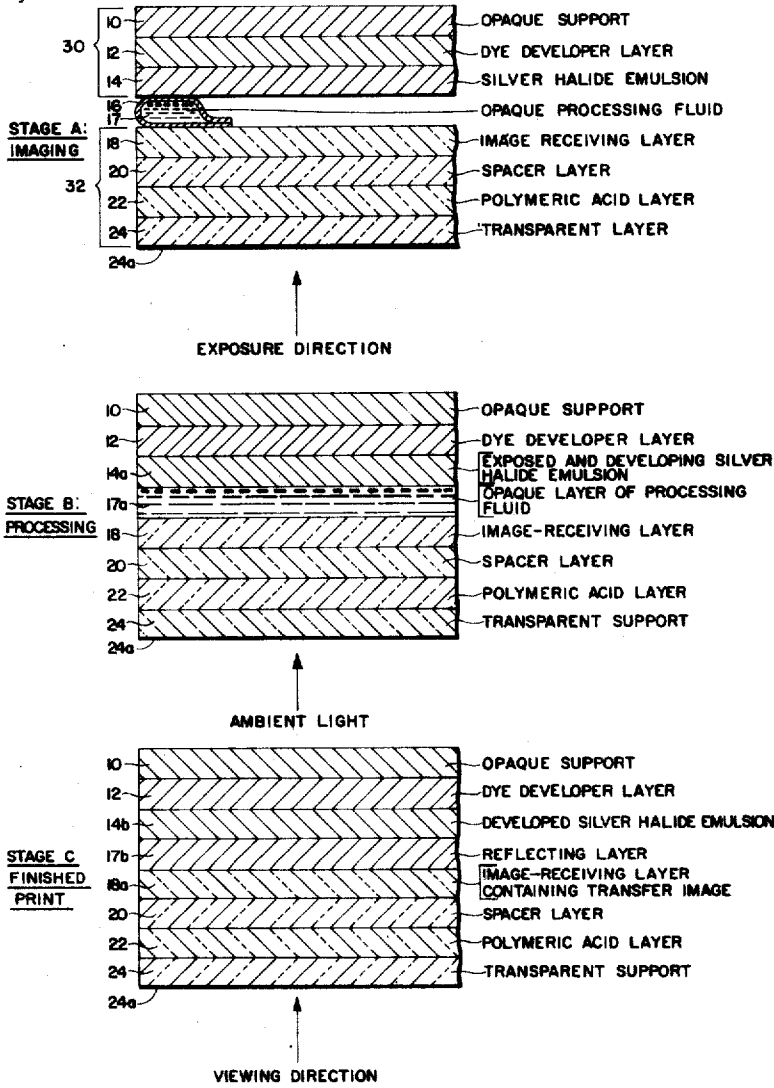
2,983,606	5/1961	Rogers.....	96/3
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3,345,163	10/1967	Land et al.....	96/3
3,351,470	11/1967	McCune.....	96/3
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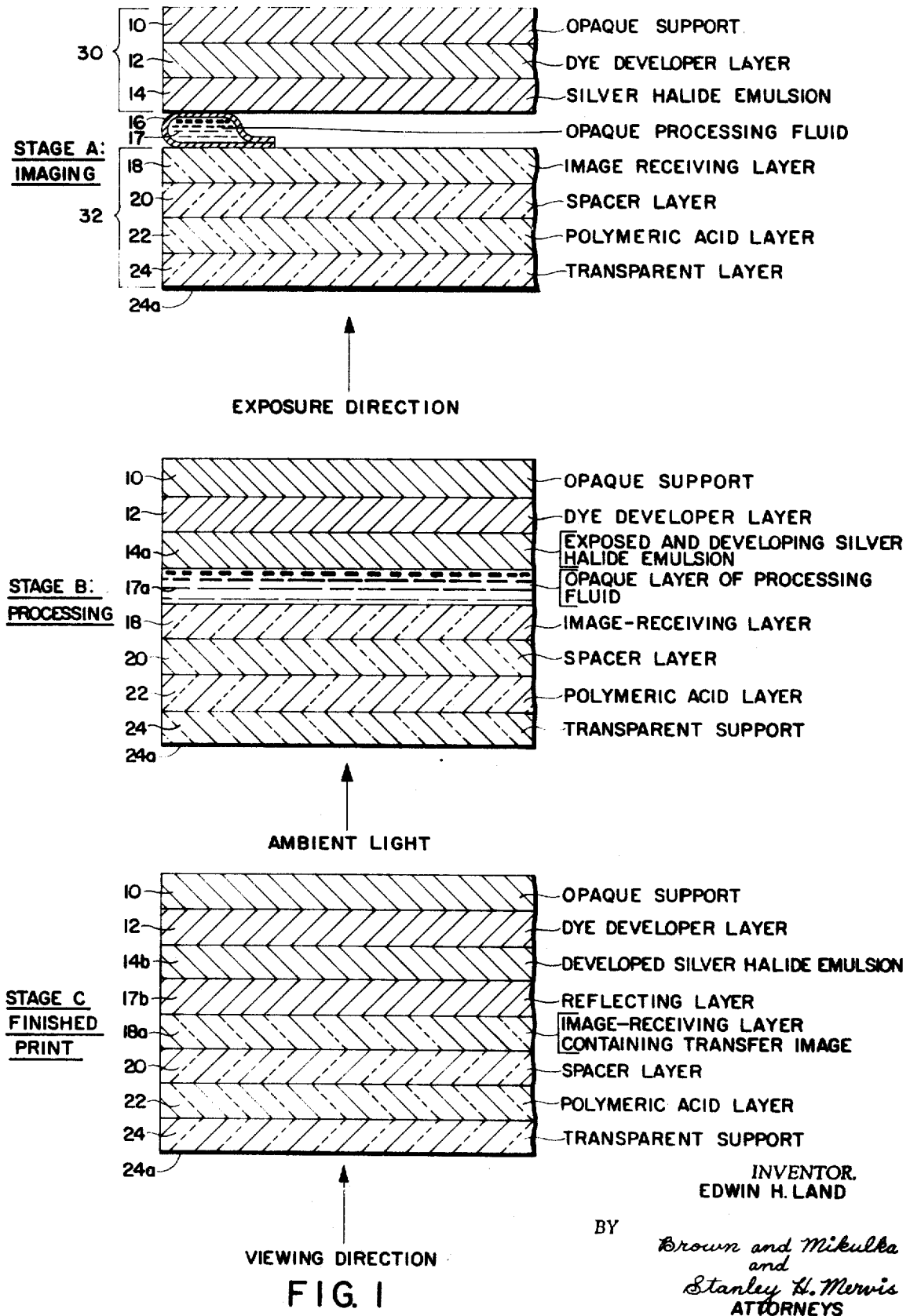
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[57] ABSTRACT

Photographic films and particularly film units for performing diffusion transfer processes, are disclosed which may be processed outside of a camera. A light-absorbing reagent is employed to prevent postexposure fogging by actinic light passing through a transparent face of the film unit. After a suitable period, the light-absorbing reagent is rendered ineffective to prevent viewing an image through said transparent face. In a preferred embodiment, the image is viewed against a light-reflecting material such as a white pigment, said light-reflecting material and said light-absorbing material being employed in combination to provide desired protection against said postexposure fogging. Particularly useful light-absorbing materials are dyes which are light absorbing at a pH at which image formation is effected and nonlight-absorbing at a subsequently attained pH. Other light-absorbing reagents including dyes which are selectively mordanted to render them ineffective to prevent viewing transfer images visible against a light-reflecting material. The final image may be dye or silver. Suitable image-forming reagents include dye developers, color couplers, coupling dyes, etc.

134 Claims, 18 Drawing Figures





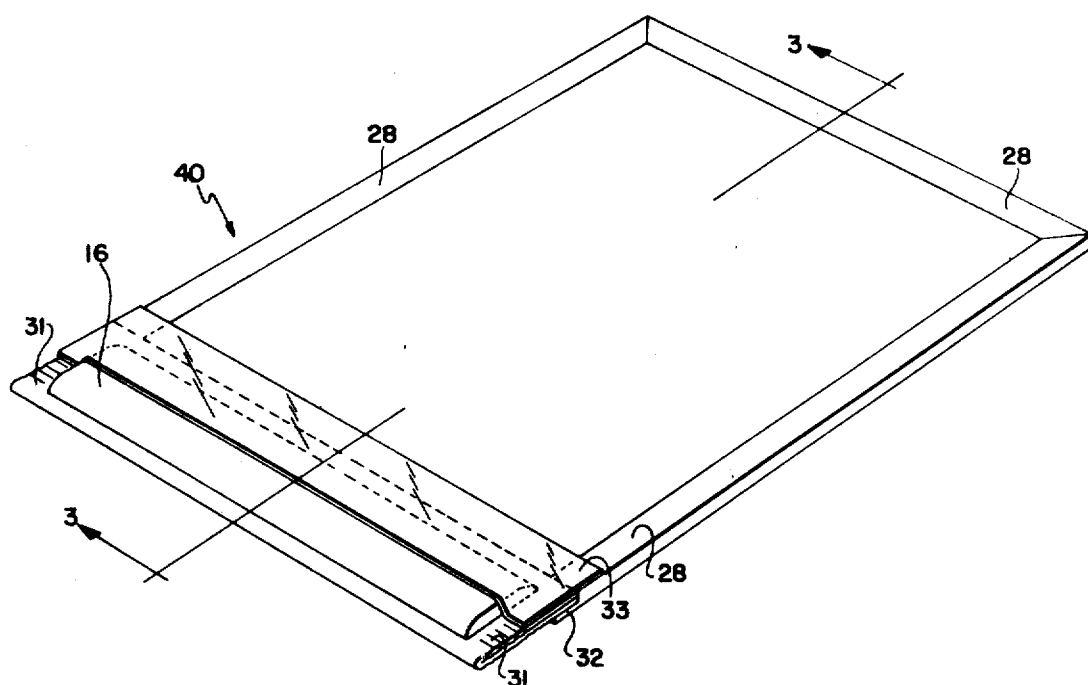


FIG. 2

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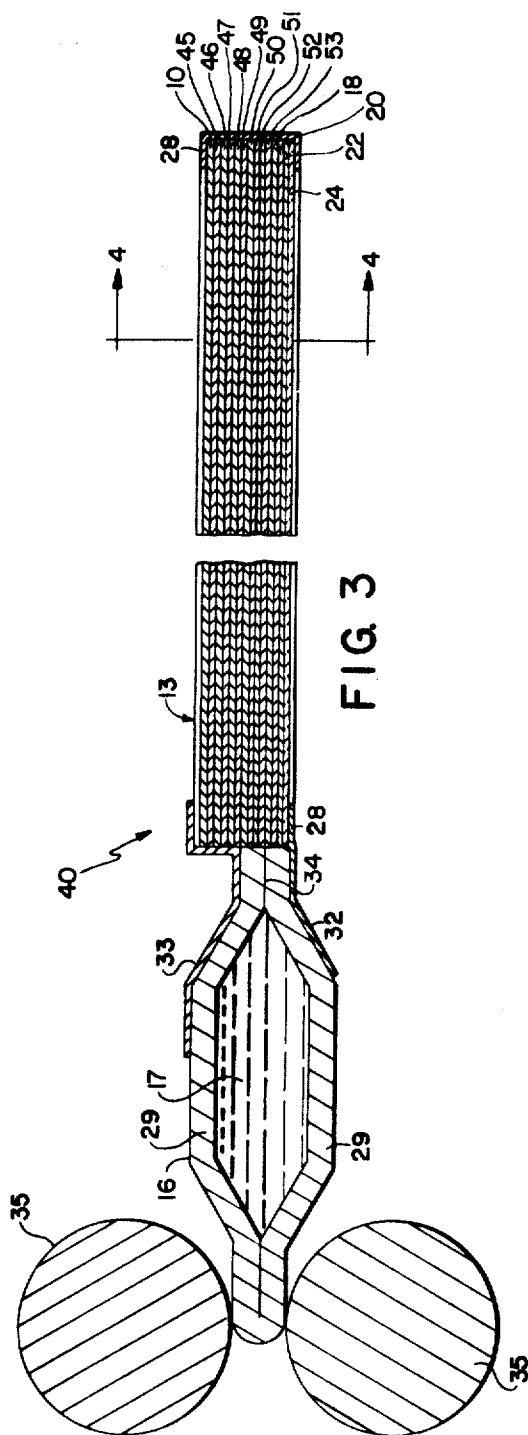


FIG. 3

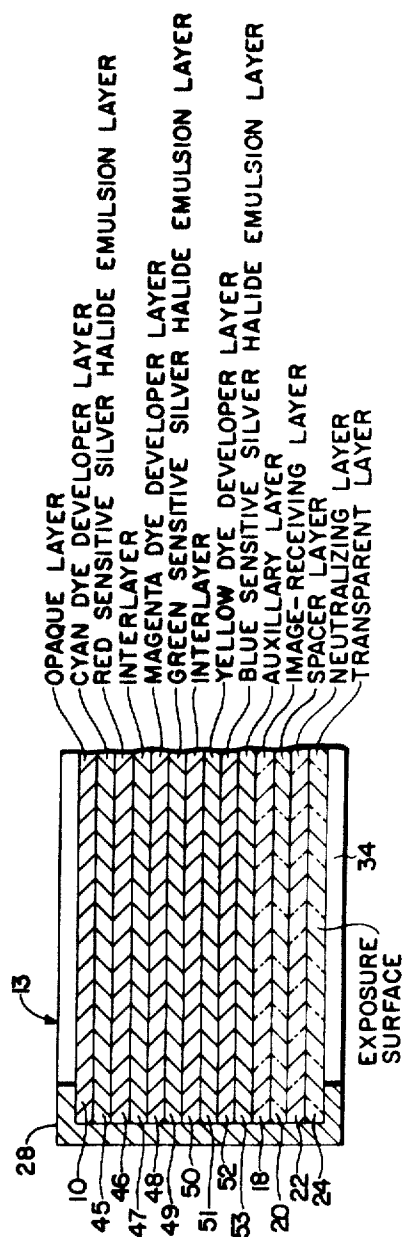


FIG. 4

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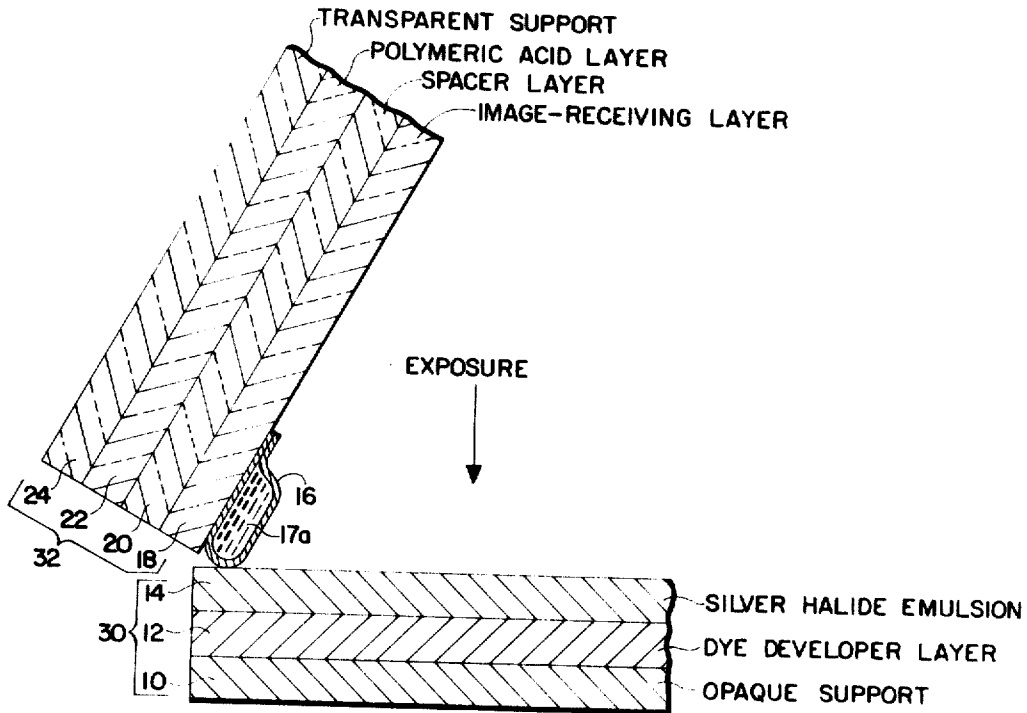


FIG. 5

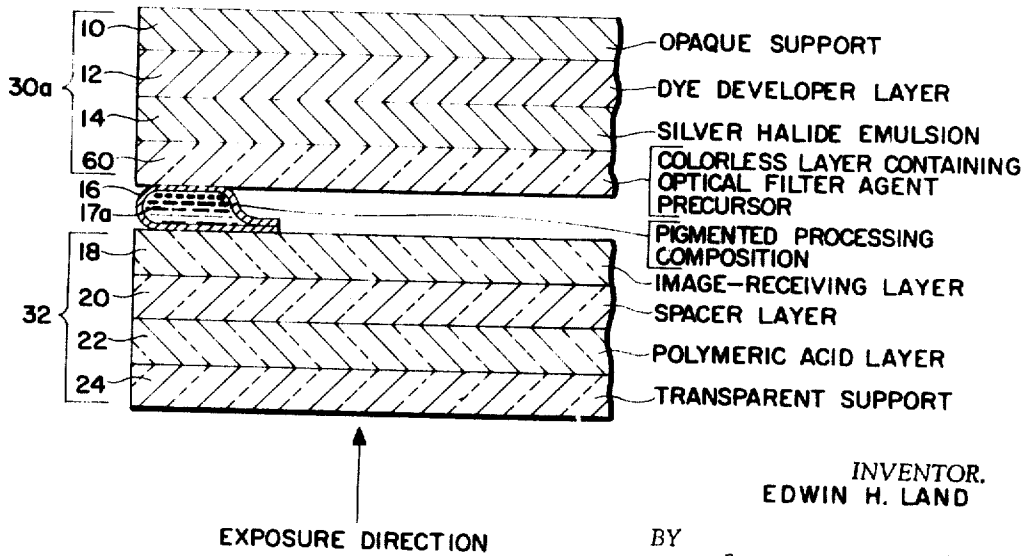


FIG. 6

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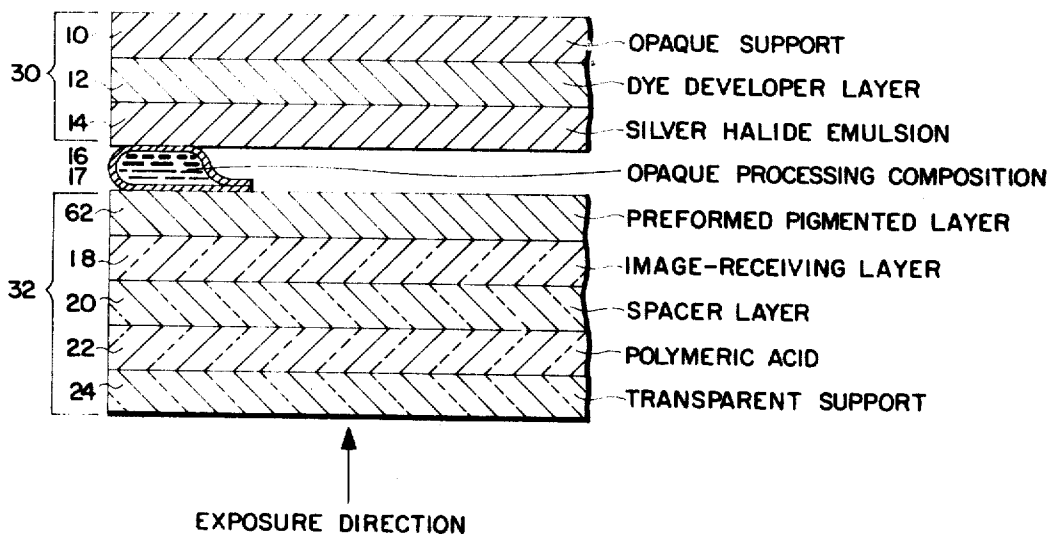
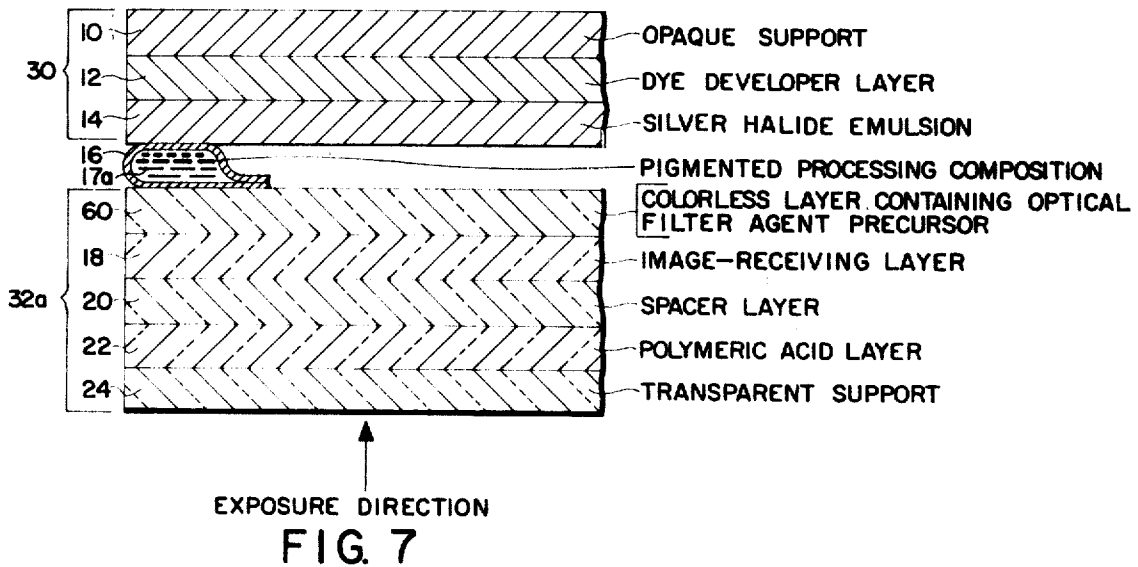
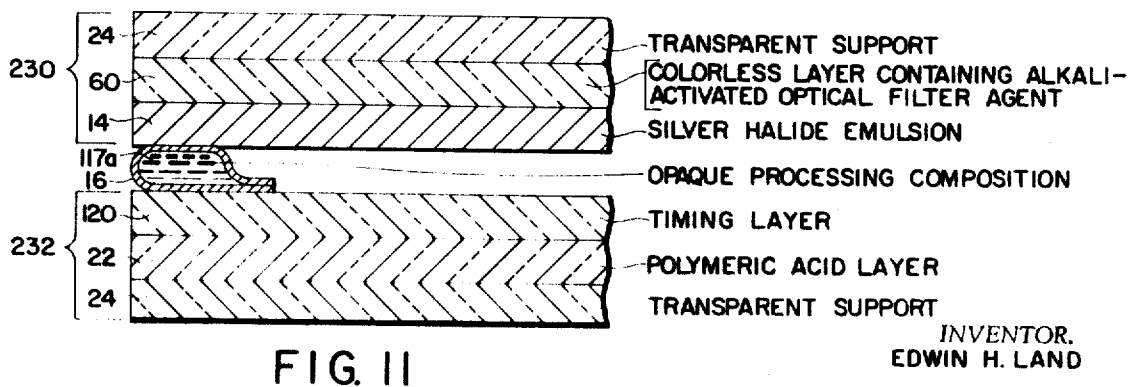
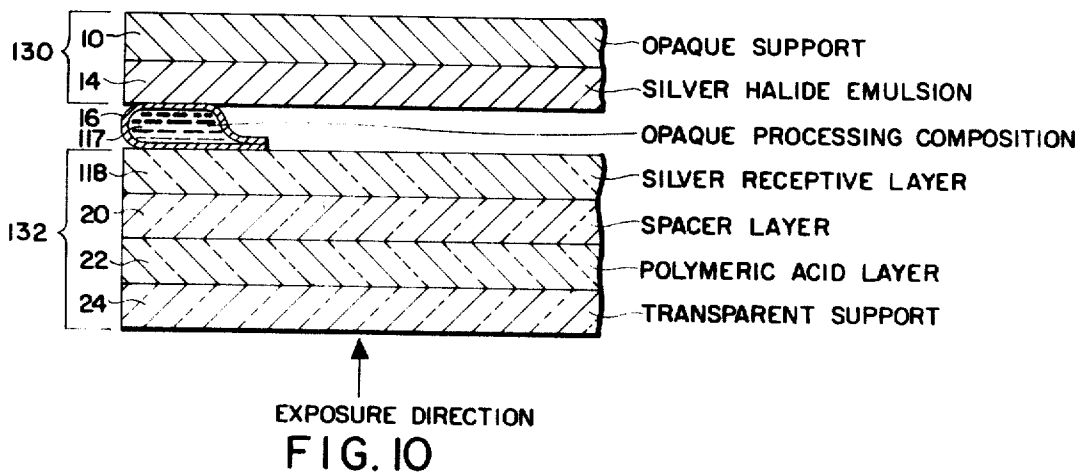
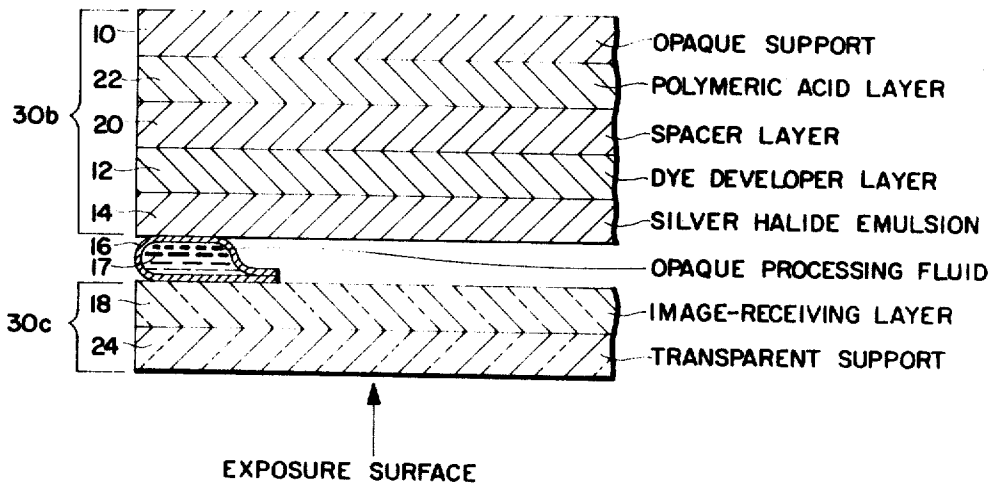


FIG. 8

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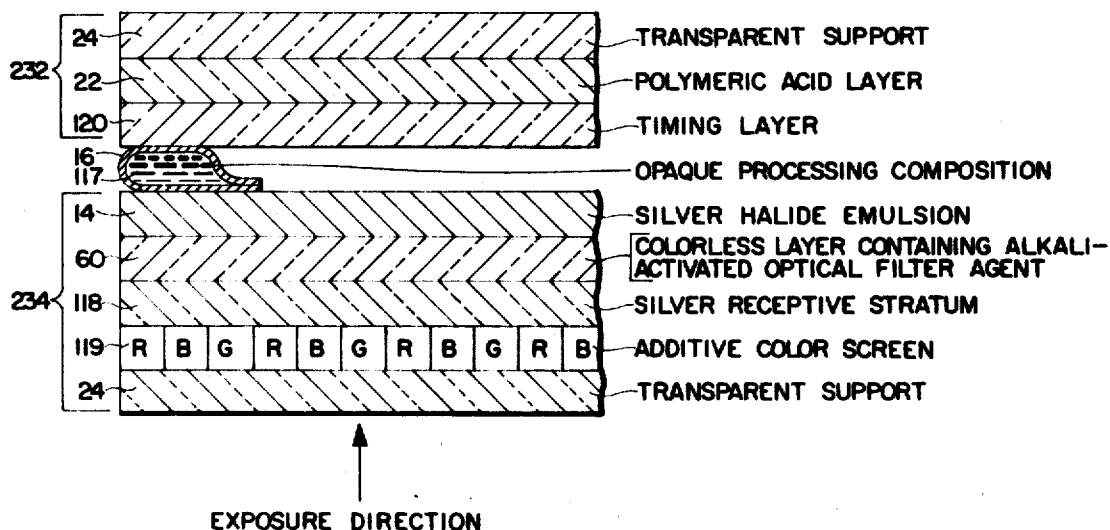


FIG. 12

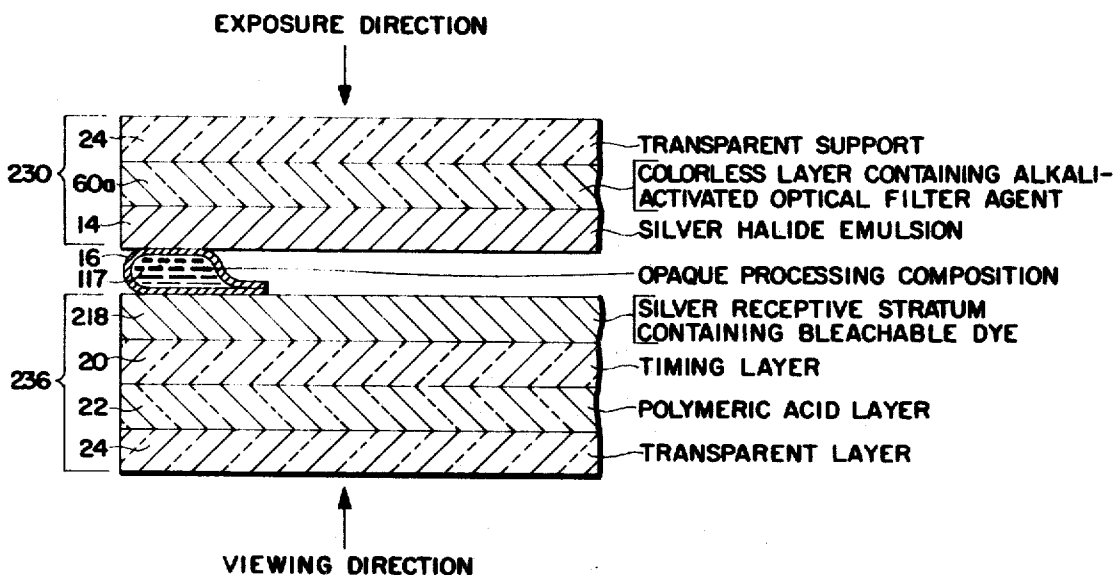


FIG. 13

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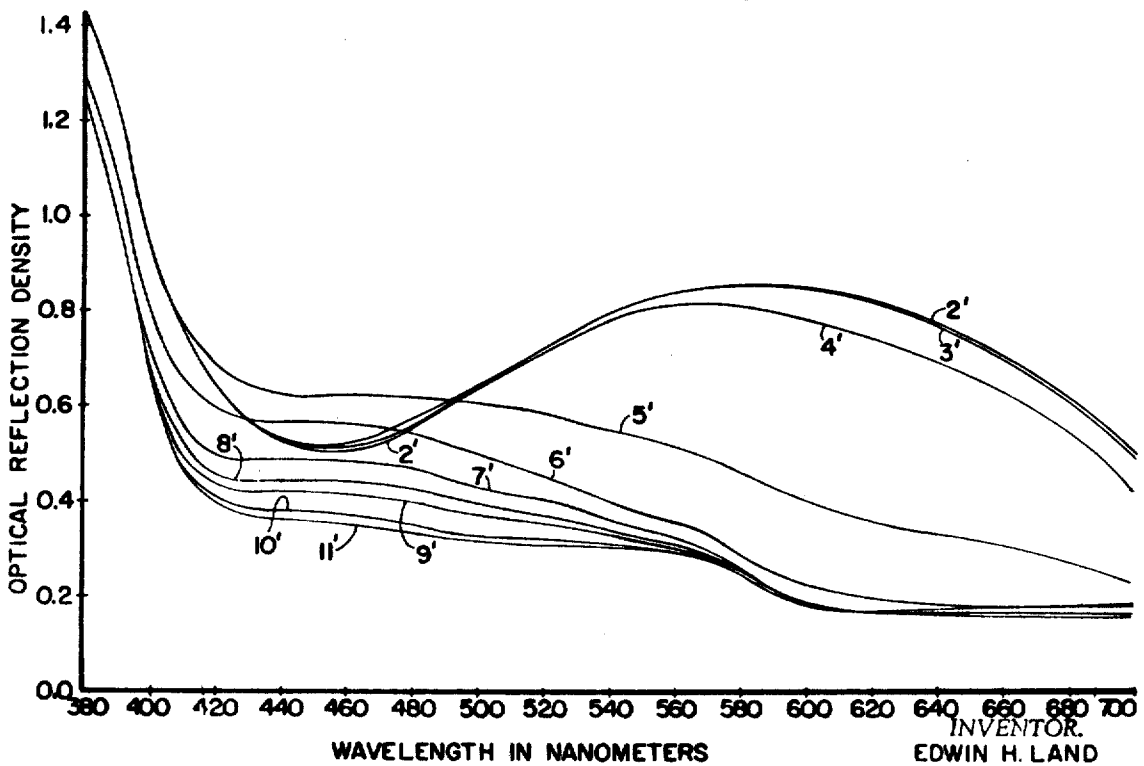
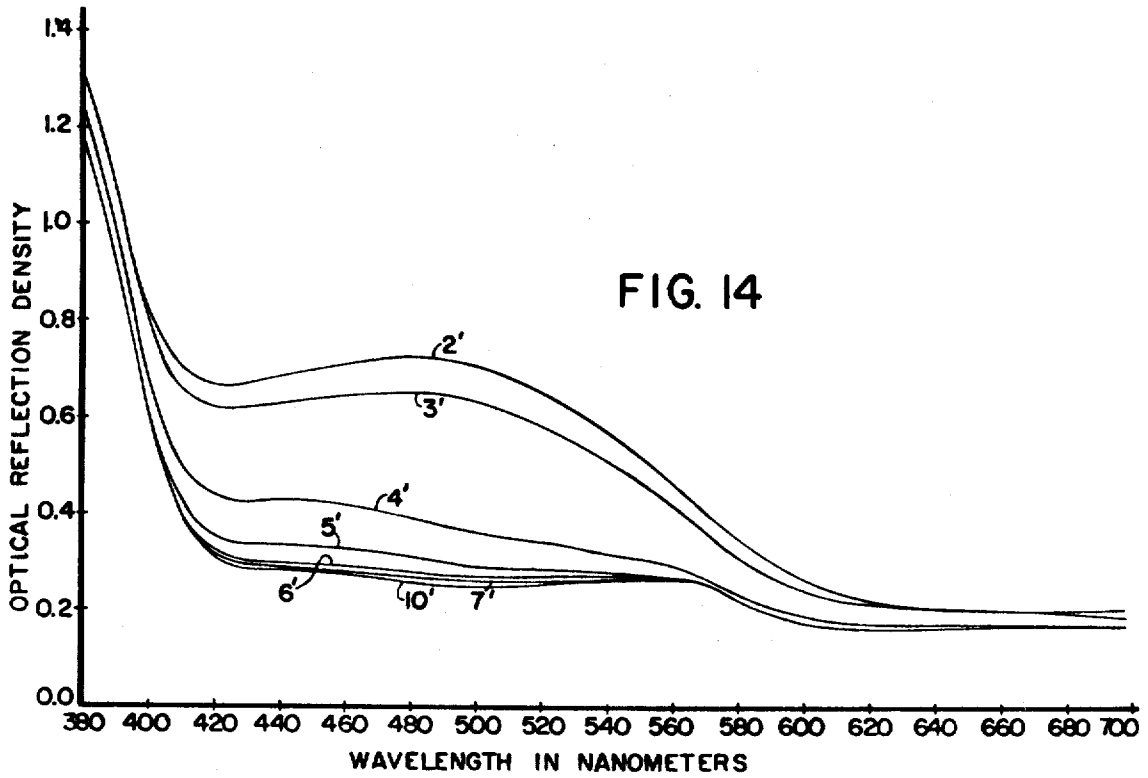


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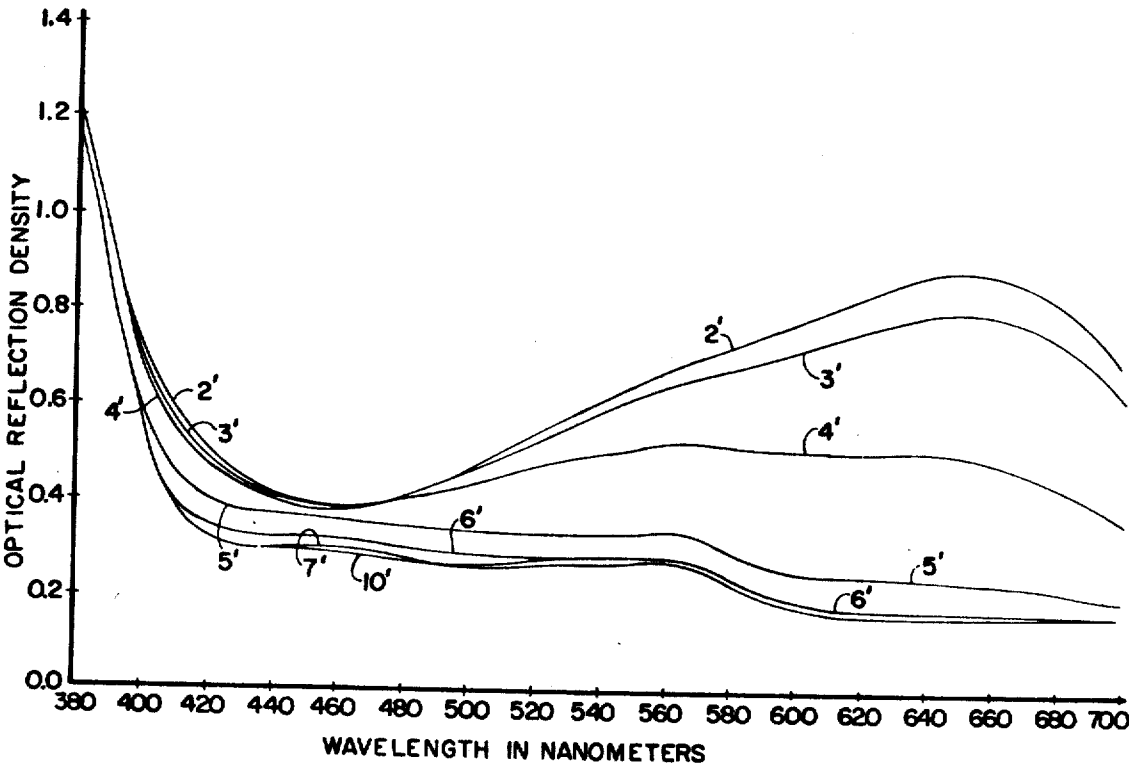


FIG. 16

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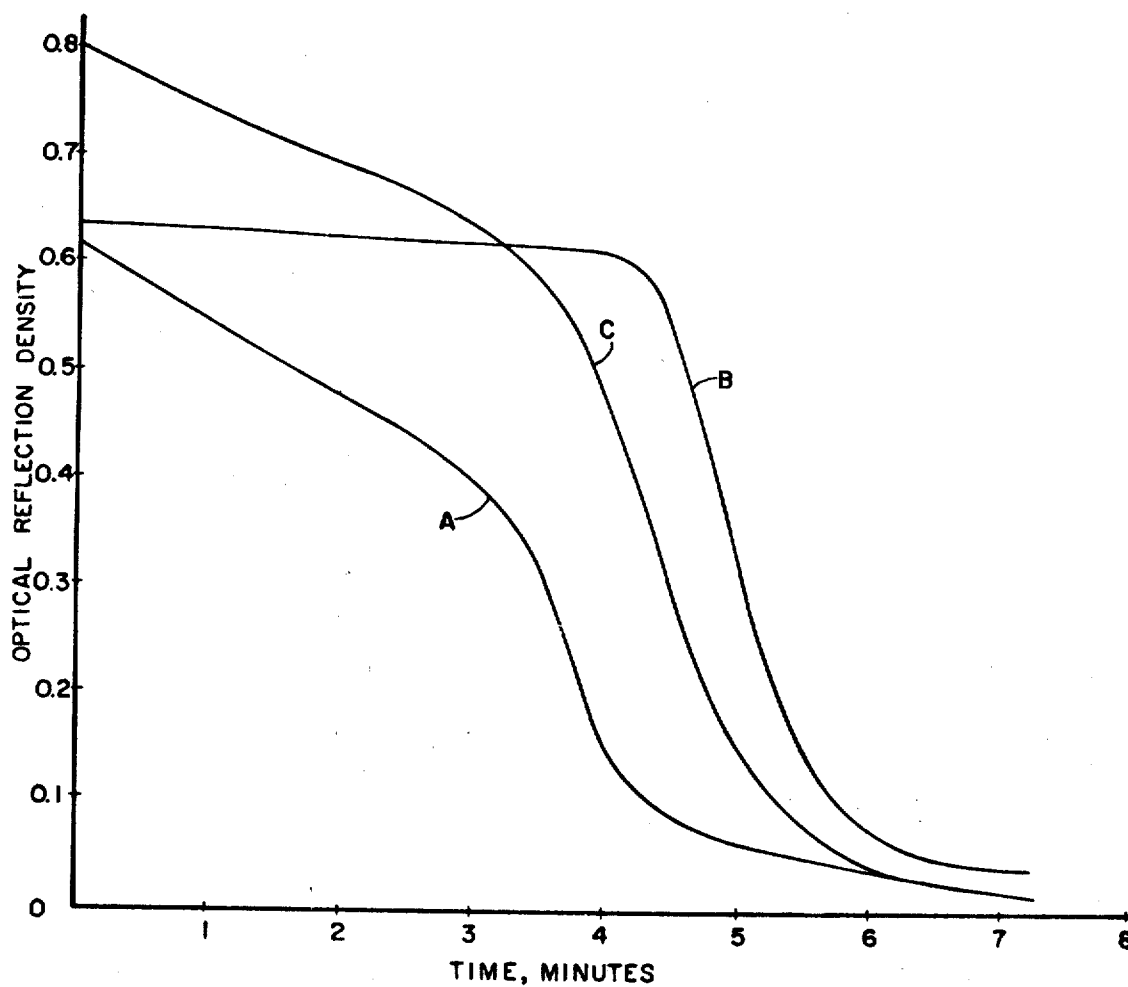


FIG. 17

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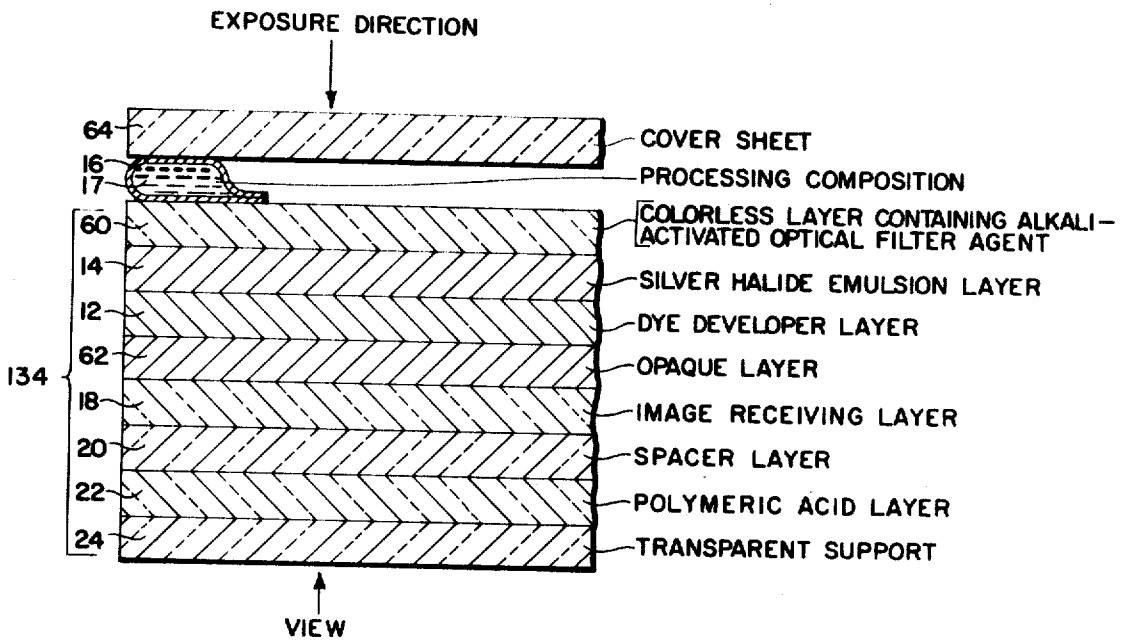


FIG. 18

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PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

This application is in part a continuation of copending application Ser. No. 786,352 filed Dec. 23, 1968, (now abandoned) and in part a continuation of copending application Ser. No. 43,782 filed June 5, 1970 (now abandoned).

This invention is concerned with photography and, more particularly, with photographic processes which are conducted outside of a camera and wherein undesired post-imaging fog is prevented by a light-absorbing reagent retained within the ultimate photograph, and with photographic products useful in performing such processes.

A number of photographic processes by which images may be developed and viewed within seconds or minutes after exposure have been proposed. Such processes generally employ a processing composition which is suitably distributed between two sheetlike elements, the desired image being carried by one of said sheetlike elements. The resulting images may be in black and white, e.g., in silver, or in one or more colors. Processing may be conducted in or outside of a camera. The most useful of such processes are the diffusion transfer processes which have been proposed for forming silver or dye images, and several of these processes have been commercialized. Such processes have in common the feature that the final image is a function of the formation of an imagewise distribution of an image-providing reagent and the diffusion transfer of said distribution to or from the stratum carrying the final image, whether positive or negative. It has also been proposed to form the final desired image in the photosensitive stratum per se by monobath processing to obtain a negative image or by so-called direct positive processing to obtain a positive image, employing processing techniques and physical film structures similar to those found useful in diffusion transfer processing. This invention is directed to providing techniques and film structures by which photographic processes, such as those noted above, may be performed, at least in part, outside of a camera.

The primary objects of this invention are to provide photographic products particularly adapted for use in instances where at least a portion of the process is performed under conditions which would ordinarily result in postexposure fogging of the photosensitive material, and more particularly for use in diffusion transfer processes performed, at least in part, outside of the light-protective confines of a camera. A further object of this invention is to provide photographic products and processes wherein a light-absorbing reagent is employed to protect a photosensitive material against postexposure fogging, during at least the early stage of image formation, by light passing through a transparent element, said light-absorbing reagent being subsequently rendered ineffective to prevent viewing said image through said transparent element. An additional object of this invention is to provide diffusion transfer processes and products employing dyes which are light absorbing at a pH at which image formation is effected and non-light-absorbing at a subsequently attained pH. Still another object of this invention is to provide photographic diffusion transfer processes and products wherein a light-reflecting material and a light-absorbing material are employed in combination to provide protection against postexposure fogging by light transmitted through a transparent element of the film unit, said light-absorbing material being rendered ineffective to prevent viewing the final image through said transparent element and against said light-reflecting material. Yet another object of this invention is to provide diffusion transfer processes and products wherein a light-absorbing material is initially so positioned as not to interfere with photoexposure but is so positioned and/or constituted as to provide protection against postexposure fogging. A further object of this invention is to provide photographic products having the aforesaid characteristics wherein the photosensitive material is exposed through a transparent element, and distribution of a processing composition provides a laminate including said photosensitive material, said transparent element and an

image-carrying layer, and the image formed in said image-carrying layer is viewed through said transparent element, the laminate being maintained as an integral entity after the process has been completed.

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

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

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

FIG. 1 is a diagrammatic enlarged cross-sectional view of a film unit embodying the invention, illustrating the arrangement of layers during the three illustrated stages of a monochrome diffusion transfer process, i.e., exposure, processing and final image;

FIG. 2 is a perspective view of a photographic film unit embodying the invention;

FIG. 3 is a diagrammatic enlarged cross-sectional view of the film unit of FIG. 2, along section line 3—3, illustrating the association of elements during the exposure stage 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;

FIG. 4 is a diagrammatic, further enlarged cross-sectional view of the film unit of FIGS. 2 and 3, along section lines 4—4, further illustrating, in detail, the arrangement of layers comprising the photosensitive laminate during the exposure stage of the transfer process;

FIG. 5 is a diagrammatic, enlarged cross-sectional view of the film unit of FIG. 1 exposed in a different manner;

FIGS. 6, 7, 8, 9 and 18 are diagrammatic, enlarged cross-sectional views of additional dye developer film units, embodying this invention, during the exposure stage;

FIG. 10 is a diagrammatic, enlarged cross-sectional view of a film unit for forming a silver transfer image and embodying this invention;

FIG. 11 is a diagrammatic, enlarged cross-sectional view of a film unit for developing a negative silver image by monobath processing and embodying this invention;

FIG. 12 is a diagrammatic, enlarged cross-sectional view of a film unit for obtaining an additive color image and embodying this invention;

FIG. 13 is a diagrammatic, enlarged cross-sectional view of a film unit for obtaining a dye image by the silver dye bleach process and embodying this invention;

FIGS. 14, 15 and 16 are each graphic illustrations of the spectral absorption characteristics of individual pH-sensitive dye filter agents employed in the practice of the present invention graphically denoting the spectral absorption/optical density relationship of the agents at specified intervals during performance of a photographic diffusion transfer process of the invention; and

FIG. 17 is a graphic illustration of the optical density/unit processing time relationship of the filter agents of FIGS. 14, 15 and 16, at their respective λ_{max} , wherein Curve A denotes the optical/density/unit processing time relationship of the filter agent of FIG. 14 Curve B denotes the relationship with respect to the filter agent of FIG. 15 and Curve C denotes the relationship with respect to the agent of FIG. 16.

As indicated above, this invention is primarily directed to photographic processes wherein the desired image is obtained by processing an exposed photosensitive material, preferably silver halide, with a processing composition distributed between two sheetlike elements, one of said elements including said photosensitive material. The processing composition is so applied and confined within and between the two sheet-

like elements as not to contact or wet outer surfaces of the superposed elements, thus providing a film unit or film packet whose external surfaces are dry. The processing composition may be viscous or nonviscous, and preferably is distributed from a single-use rupturable container; such pressure rupturable processing containers are frequently referred to as "pods." The final image may be black and white, monochrome or multicolor and either negative or positive with respect to the photographed subject. The present invention is especially, if not uniquely, adapted for facilitating processing outside of a camera film units which are maintained as an integral laminate after processing, the desired image being viewed through one face of said laminate.

In diffusion transfer embodiments of this invention the diffusible image-providing substance may be a complete dye or a dye intermediate, e.g., a color coupler. The preferred embodiments of this invention use a dye developer, that is, a compound which is both a silver halide developing agent and a dye. As disclosed in U.S. Pat. No. 2,983,606, issued May 9, 1961 to Howard G. Rogers, a photosensitive element containing a dye developer and a silver halide emulsion may be exposed and wetted by a liquid processing composition, for example, by immersion, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition, positioned intermediate the photosensitive element and the image-receiving layer, permeates the emulsion to initiate development of the latent image contained therein. The dye developer is immobilized or precipitated in exposed areas as a consequence of the development of the latent image. This immobilization is apparently, at least in part, due to a change in the solubility characteristics of the 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 emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer, diffusible in the liquid processing composition, as a function of the point-to-point degree of exposure of the silver halide 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 layer receives a depthwise diffusion, from the developed emulsion, of unoxidized dye developer without appreciably disturbing the imagewise distribution thereof to provide a reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. In a preferred embodiment of said U.S. Pat. No. 2,983,606 and in the commercial applications thereof, the desired positive image is revealed by separating the image-receiving layer from the photosensitive element at the end of a suitable imbibition period. Alternatively, as also disclosed in said U.S. Pat. No. 2,983,606, the image-receiving layer need not be separated from its superposed contact with the photosensitive element, subsequent to transfer image formation, if the support for the image-receiving layer, as well as any other layers intermediate said support and image-receiving layer, is transparent and a processing composition containing a substance, e.g., a white pigment, effective to mask the developed silver halide emulsion or emulsions is applied

between the image-receiving layer and said silver halide emulsion or emulsions.

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

Multicolor images may be obtained using color image-forming components such as, for example, dye developers, in diffusion transfer processes by several techniques. One such technique contemplates obtaining multicolor transfer images utilizing dye developers by employment of an integral multilayer photosensitive element, such as is disclosed in the aforementioned U.S. Pat. No. 2,983,606, and particularly with reference to FIG. 9 of the patent's drawing, and also in U.S. Pat. No. 3,345,163 issued Oct. 3, 1967 to Edwin H. Land and Howard G. Rogers, wherein at least two selectively sensitized photosensitive strata, superposed on a single support, are processed, simultaneously and without separation, with a single common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion stratum, for example, in the form of particles, or it may be disposed in a stratum behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata are disclosed to be optionally separated from other sets by suitable interlayers, for example, by a layer or stratum of gelatin or polyvinyl alcohol. In certain instances, it may be desirable to incorporate a yellow filter in front of the green-sensitive emulsion and such yellow filter may be incorporated in an interlayer. However, where desirable, a yellow dye developer of the appropriate spectral characteristics and present in a state capable of functioning as a yellow filter may be so employed and a separate yellow filter omitted.

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

As examples of materials for use as the image-receiving layer, mention may be made of solution dyeable polymers such as nylons 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.

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 c.p.s. at a temperature of approximately 24° C. and preferably in the order of 100,000 c.p.s. to 200,000 c.p.s. at that temperature.

Diffusion transfer processes which have been commercialized for camera use originally required a dark chamber within the camera structure wherein the requisite imbibition and diffusion transfer could occur with little or no danger of further exposure. Subsequent commercial embodiments have permitted the film unit to be removed from the camera (thereby eliminating the dark chamber and reducing the size and weight of the camera) without fogging the developing photosensitive material by use of opaque supports to protect against light incident thereon; fogging by internal reflection within a layer of such film units, if a problem, could be controlled, e.g., by incorporation of a small quantity of carbon black in the processing fluid and/or a small quantity of a white pigment, e.g., titanium dioxide, in appropriate layer or layers of the image-receiving element, as disclosed in U.S. Pat. No. 3,351,470 issued Nov. 7, 1967 to William J. McCune, Jr.

In the last-noted embodiments, the image-receiving element had to be separated from the processed photosensitive element in order to view the transfer image otherwise hidden from view by the opaque supports.

A marked reduction in the amount of required materials constituting the film pack or roll, is possible if the superposed photosensitive and image-receiving layers are maintained as a laminate after formation of the desired transfer image. Such a structure, however, requires that the support for the image-receiving layer be transparent, rather than opaque, so that the transfer image may be viewed without separating the film lamination. This invention is primarily directed to facilitating the processing of such film units outside of a camera without fogging of the photosensitive material as a consequence of light incident upon said transparent support. In its preferred embodiments, this invention is especially directed to diffusion transfer processes providing a finished print comprising a laminate containing a visible transfer image and one or more developed photosensitive, e.g., silver halide, strata separated from the stratum containing the desired visible image by appropriate masking means, preferably a reflecting layer comprising a white pigment, e.g., titanium dioxide.

U.S. Pat. Nos. 3,415,644, 3,415,645 and 3,415,646, all issued Dec. 10, 1968 in the name of Edwin H. Land, disclose and claim photographic products and processes wherein a photosensitive element and an image-receiving element are maintained in fixed relationship prior to exposure, and this relationship is maintained as a laminate after processing and image formation. In these processes, the final image is viewed through a transparent (support) element against a reflecting, i.e., white background. In a particularly useful embodiment, photoexposure is made through said transparent element and application of the processing composition provides a layer of light-reflecting material to provide a white background. The light-reflecting material (referred to in said patents and appli-

cations as an "opacifying agent") is preferably titanium dioxide, and it also performs an opacifying function, i.e., it is effective to mask the developed silver halide emulsions so that the transfer image may be viewed without interference therefrom, and it also helps to protect the photoexposed silver halide emulsions from postexposure fogging by light passing through said transparent layer if the photoexposed film unit is removed from the camera before image formation is completed. The present invention is directed to improvements in the processes and products disclosed in the said patents and is particularly directed to providing light-absorbing materials effective to permit performing said processes outside of the camera in which photoexposure is effected. For convenience, the specifications of the said patents and applications are hereby specifically incorporated herein.

In accordance with this invention, a light-absorbing material or reagent, preferably a dye, is provided so positioned and/or constituted as not to interfere with photoexposure but so positioned between the photoexposed silver halide emulsions and the transparent support during processing after photoexposure as to absorb light which otherwise might fog the photoexposed emulsions. Furthermore, the light-absorbing material is so positioned and/or constituted after processing as not to interfere with viewing the desired image shortly after said image has been formed. In the preferred embodiments, the light-absorbing material, also sometimes referred to herein as an optical filter agent, is initially contained in the processing composition together with a light-reflecting material, e.g., titanium dioxide.

The concentration of indicator dye is selected to provide the optical transmission density required, in combination with other layers intermediate the silver halide emulsion layer(s) and the incident radiation, to prevent nonimagewise exposure, i.e., fogging, by incident actinic light during the performance of the particular photographic process. It has been found, by interposing neutral density (carbon containing) filters over a layer of titanium dioxide, that a transmission density of approximately 6.0 from said neutral density filters was effective to prevent fogging of a diffusion transfer multicolor film unit of the type described in said U.S. Pat. No. 3,415,644 having a transparent support layer and an Equivalent ASA Exposure Index of approximately 75 when processed for 1 minute in 10,000 foot candles of color-corrected light, a light intensity approximately the intensity of a noon summer sun. The transmission density required to protect such a film unit under the stated conditions may also be expressed in terms of the "system" transmission density of all the layers intermediate the silver halide layer(s) and the incident light; the "system" transmission density required to protect a color film unit of the aforementioned type and photographic speed has been found to be on the order of 7.0 to 7.2. Lesser levels of optical transmission density would, of course, provide effective protection for shorter processing times, lesser light intensities and/or films having lower exposure indices. The transmission density and the indicator dye concentration necessary to provide the requisite protection from incident light may be readily determined for any photographic process by following the above-described procedure or obvious modifications thereof. It will be recognized that a particular transmission density may not be required for all portions of the spectrum, lesser density being sufficient in wavelength regions corresponding to lesser sensitivities of the particular photosensitive material.

In a particularly useful embodiment, the light-absorbing dye is highly colored at the pH of the processing composition, e.g., 13-14, but is substantially nonabsorbing of visible light at a lower pH, e.g., less than 10-12. This pH reduction may be effected by an acid-reacting reagent appropriately positioned in the film unit, e.g., in a layer between the transparent support and the image-receiving layer, as described in more detail below. Such a color-changing dye may be initially positioned in a layer of the film unit through which photoexposure is effected if it is incorporated under conditions, e.g., pH, such that it will not absorb visible light (intended to expose the

silver halide emulsions) until after application of an alkaline processing composition.

It will be understood that if the final form of the light-absorbing material at the completion of processing should be colored, it should not be present in the image-receiving layer or in any other layer where it would interfere with viewing of the transfer image through the transparent element or adversely affect the properties of said image. This result is readily obtained if the light-absorbing material is substantially colorless at the final pH of the involved layers, although suitable precautions obviously should be exercised to exclude it from the image-receiving layer if it may have an adverse effect upon the stability of the image over a prolonged period of time. If the light-absorbing dye is colored at the final pH, it may be excluded from view by mordanting it in a layer of the laminate on the opposite side of the light-reflecting layer from the layer containing the transfer image. This result may be obtained by using light-absorbing dyes which, e.g., mordant to the silver halide emulsion layer, preferably to the gelatin thereof, but not in the layers intermediate the transparent support and the light-reflecting layer.

It will be understood that the optical filter agent contemplated by this invention may be present, in whole or in part, in the light-reflecting layer when image formation is completed if it does not absorb visible light at that stage of the process. Accordingly, the optical filter agents herein contemplated may be readily distinguished from insoluble materials such as carbon black disclosed in the aforesaid patents and applications as an additive in small amounts to increase the light-protective properties of a titanium dioxide light-reflecting layer while retaining the white appearance of the titanium dioxide layer.

It will be understood that a mixture of light-absorbing materials may be used so as to obtain absorption in all critical areas of the visible and near-visible by which the silver halide emulsions, e.g., a panchromatic black-and-white silver halide emulsion or a multicolor silver halide photosensitive element, being used are exposable. Many dyes which change from colorless to colored as a function of pH, e.g., the various phthalein dyes, are known and appropriate selection may be made by one skilled in the art to meet the particular conditions of a given process and film unit. Dyes which change from colorless to colored as a function of pH are frequently referred to in the chemical and related arts as indicator dyes. If a given dye exhibits instability if stored for a period of time within a pod containing the processing composition, such a dye may be used by employing a double-compartmented rupturable pod, or two associated rupturable pods, such that the dye is stored separate from, e.g., the alkali, and the complete processing composition containing said dye is constituted at the time of use, in accordance with techniques well understood in the art.

It is also contemplated to utilize as optical filter agents dyes included in the processing composition (so as not to interfere with photoexposure) which are not colorless at the final pH of the process provided such dyes are so positioned at the end of the process as to be masked by a white reflecting layer, e.g., said optical filter agents are diffused from or through the stratum providing the white reflecting layer to a stratum containing a preferential mordant for said optical filter agent. Indeed, it is also within the scope of this invention to utilize such "behind the reflecting layer" preferential mordanting with dyes which do undergo a color change as a function of pH; this embodiment facilitates the use of dyes which "clear," i.e., change from colored to colorless, more slowly than would otherwise be desirable, e.g., from the standpoint of early viewing of the transfer image without sacrificing protection of the developing photosensitive strata. The mordant for the optical filter agent should be so positioned as to retain the optical filter agent physically in a position within the film unit effective to protect the developing photosensitive strata from further exposure. Thus, this mordant is preferably located in a stratum positioned between the photosensitive strata and the reflecting layer.

As noted above, the optical filter agent may be initially positioned in a layer of the film unit, i.e., in a stratum positioned between the image-receiving layer and the photosensitive strata (e.g., in a stratum coated over either the image-receiving layer or the first photosensitive layer upon which light would be incident) in a form such that it was essentially colorless until a processing composition was applied. Thus, a pH-sensitive dye which is colorless at an acidic pH may be incorporated in a nondiffusible form in an acid state in a stratum of the film unit positioned as indicated above; application of an alkaline processing composition is effective to transform said pH-sensitive dye into its colored or light-absorbing form. This "filter color generation" step should be rapid and provide light-absorbing capability effective to provide the desired light protection when the film unit is removed from the camera. The time span between application of the alkaline processing composition and exit of the film unit from the dark into the light is a function of the distance from the point at which the processing composition is applied to the exit point from the camera, the rate at which the film unit is advanced, and the rate at which the alkali is effective to render the pH-sensitive dye colored; these rates may be adjusted with respect to each other, together with the selection of the particular pH-sensitive dye or dyes, so as to provide useful light filtering for a given photographic system.

Instead of using a pH-sensitive dye in a colorless state, it is possible to use an optical filter agent precursor which is colorless as incorporated in the film unit but which becomes highly colored upon reaction with a reagent contained in the processing composition or dissolved by the processing composition from a layer of the film unit and thus made available for reaction with said optical filter agent precursor. As examples of such materials, mention may be made of chelatable organic compounds which are essentially colorless until chelated with an appropriate metal, the former being initially positioned in a layer of the film unit and the latter contained in the processing composition as a soluble metal salt capable of undergoing the desired chelation reaction.

It will therefore be seen that this invention contemplates the use of optical filter agents which are (a) initially colored and located out of the photoexposure optical path for the photosensitive material, or initially colorless if located in said optical path, (b) located in said optical path after photoexposure, and (c) may remain in the film unit after processing without interfering in the viewing of the finished image by virtue of their becoming colorless or, if colored, their final location within the film laminate being such that they are masked from view by a reflecting layer.

In those embodiments of this invention which employ a pH reduction to "discharge" the optical filter agent, e.g., to reduce the pH to a level at which the optical filtering agent is essentially colorless, this pH reduction may be effected and controlled timewise by use of a stratum containing a suitable acid. This "acid stratum" or "neutralizing stratum" is preferably composed of a nondiffusible acid and more preferably a polymeric acid, possibly blended with one or more polymers to provide the desired concentration, distribution and availability of the acidic functional groups. Such acid strata may be referred to hereinafter for convenience as polymeric acid strata since polymeric acids are the preferred species. U.S. Pat. No. 3,362,819, issued Jan. 9, 1968 to Edwin H. Land, describes and claims diffusion transfer image-receiving elements comprising a support layer possessing on one surface thereof, in sequence, a polymeric acid layer and an image-receiving layer adapted to provide a visible image upon transfer to said layer of diffusible dye image-forming substance, and most preferably include an inert timing or spacer layer intermediate the polymeric acid layer and the image-receiving layer.

As set forth in U.S. Pat. No. 3,362,819 the polymeric acid layer comprises 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. In the preferred embodiments disclosed, the acid polymer contains free carboxyl 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 said patent, mention may be made of dibasic acid half-ester derivatives or 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 of cellulose modified with sulfoanhydrides, e.g., with orthosulfobenzoic 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.

The acid polymer layer should contain at least sufficient acid groups to effect a reduction in the pH of the image layer from a pH of about 13 to 14 to a predetermined pH, e.g., 11 or lower, to a pH of about 5 to 8 within a short time. The "predetermined pH" is a function of the processing time required to form the desired image after which point pH reduction acids in terminating further photographic processing, the time period after which light protection is not required, and the pH at which the optical filter agent's color is discharged.

It is, of course, necessary that the action of the polymeric acid be so controlled as not to interfere with either development of the negative or image transfer. For this reason, the pH of the image layer preferably is kept at a level of pH 12 to 14 until the dye image has been formed after which the pH is reduced very rapidly to at least about pH 11, and preferably about 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 usually necessary that the pH of the image layer remain on the order of 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. The processing technique thus effectively minimizes changes in image quality, e.g., color balance, as a result of the photosensitive element remaining laminated to the image-receiving layer.

In order to prevent premature pH reduction during transfer processing, as evidenced, for example, for an undesired reduction in positive image density or premature discharge of the optical filter agent, the acid groups are so distributed in the acid 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 acid polymer layer may be effected

by mixing the acid polymer with a polymer free of acid groups, or lower in concentration of acid groups, and compatible therewith, or by using only the acid polymer but selecting one having a relatively lower proportion of acid groups. These embodiments are illustrated, respectively, in the cited patent, 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 phthalyl groups than the first-mentioned cellulose acetate hydrogen phthalate.

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 may be employed to help the various polymeric layers adhere to each other during storage and use.

The inert spacer layer, 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 was 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 said 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 issued July 15, 1969 in the names of Leonard C. Farney, Howard G. Rogers and Richard W. Young, 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 transversing an inert spacer layer possessing permeability to alkali optimized to be effective within 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 increasing permeability at lower temperatures, and decreasing permeability at higher temperatures (than room temperature), 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 oxazolidinone, 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 alcohol were stated to generally comprise saturated aliphatic hydrocarbon chains of a molecular weight of at least 1,000, preferably of about 1,000 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 hydroxyl 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.

In lieu of using a polymeric acid layer adjacent the image-receiving layer, as described in said U.S. Pat. No. 3,362,819, it is also within the scope of this invention to position such a polymeric acid layer, or a second such polymeric acid layer, adjacent the support carrying the photosensitive and image-providing reagent strata, as described in U.S. Pat. No. 3,362,821 issued Jan. 9, 1968.

This invention is applicable to a wide variety of photographic processes as will be readily apparent to one skilled in the art. Dye developers are preferred image-providing substances, as indicated above, and constitute an example of initially diffusible dye image-providing substances. Other useful dye image-providing substances include initially diffusible dyes useful as image dyes per se and which couple with the oxidation product of a silver halide developing agent to provide a nondiffusible product, initially diffusible color couplers which couple with the oxidation product of a silver halide developing agent to provide image dyes, initially nondiffusible compounds which couple with the oxidation product of a silver halide developing agent to release a diffusible dye useful as an image dye per se, and initially nondiffusible dyes which upon oxidation undergo an intramolecular ring closure to release a diffusible dye useful as an image dye per se. The final image may be formed as a result of the diffusion transfer of a soluble complex of undeveloped silver halide, in which event the image may be in silver or the transferred silver halide complex may be utilized as an intermediate in the formation of an image in dye, e.g., by using the transferred silver to catalyze the bleaching of a dye thus providing an image in terms of unreacted dye. Alternatively, the transferred silver halide complex may be used to cause an initially nondiffusible coupling dye or ring-closing dye to undergo reaction to provide diffusible products which are removed from the image layer by diffusion to provide an image in terms of unreacted dye. A number of these image-forming systems will be discussed in more detail hereinafter.

Reference is now made to the accompanying drawings wherein a plurality of embodiments of this invention are illustrated and wherein like numbers, appearing in the various figures, refer to like components.

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

The optical filter agent is retained within the final film unit laminate and is preferably colorless in its final form, i.e., ex-

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

The reflecting layer provided in the embodiment of this invention shown in FIG. 1 is formed by solidification of a stratum of pigmented processing composition distributed after exposure. It is also within the scope of this invention to provide a preformed pigmented layer, e.g., coated over the image-receiving layer 18, and to effect photoexposure therethrough, in accordance with the teachings of the copending application of Edwin H. Land, Ser. No. 846,441 filed July 31, 1969 now U.S. Pat. No. 3,615,421 issued Oct. 26, 1971.

In the embodiment illustrated in FIG. 1, photo-exposure is effected through the image-receiving element. While this is a particularly useful and preferred embodiment, especially where the photosensitive element and the image-receiving element are secured together as shown in FIGS. 2, 3 and 4, it will be understood that the image-receiving element may be initially positioned out of the exposure path as illustrated in FIG. 5 and superposed upon the photosensitive element after photoexposure.

FIG. 2 sets forth a perspective view of a particularly preferred film unit, designated 40, and each of FIGS. 3 and 4 illustrate diagrammatic cross-sectional views of film unit 40, along the stated section lines 3—3 and 4—4, during the various depicted stages in the performance of a photographic diffusion transfer process as detailed hereinafter.

Film unit 40 comprises rupturable container 16, retaining, prior to processing, aqueous processing composition 17, and photosensitive laminate 13 including, in order, dimensionally stable opaque support layer 10, preferably an actinic radiation-opaque flexible sheet material; cyan dye developer layer 45; red-sensitive silver halide emulsion layer 46; interlayer 47; magenta dye developer layer 48; green-sensitive silver halide emulsion layer 49; interlayer 50; yellow dye developer layer 51; blue-sensitive silver halide emulsion layer 52; auxiliary layer 53, which may contain an auxiliary silver halide developing agent; image-receiving layer 18; spacer layer 20; neutralizing layer 22; and dimensionally stable transparent layer 24, 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 18 and the silver halide emulsion layer next adjacent thereto, for example, image-receiving layer 18 and auxiliary layer 53 as illustrated in FIGS. 3 and 4 should be less than that exhibited at the interface between the opposed surfaces of remainder of the layers forming the laminate, in order to facilitate distribution of processing solution 17 intermediate the stated image-receiving layer 18 and the silver halide 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 53 and 18 during distribution of processing composition 17 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 17 intermediate image-receiving layer 18 and the

silver halide emulsion layer next adjacent thereto, upon application of compressive pressure to pod 16 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 16 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 17 is retained. The longitudinal marginal seal 36 is made weaker than the end seals 31 so as to become unsealed in response to the hydraulic pressure generated within the fluid contents 17 of the container by the application of compressive pressure to walls 29 of the container, e.g., by passing the film unit 40 between opposed pressure applying rollers 35.

As illustrated in FIGS. 2, 3 and 4, container 16 is fixedly positioned and extends transverse a leading edge of photosensitive laminate 13 whereby to effect unidirectional discharge of the container's contents 17 between image-receiving layer 18 and the stated layer next adjacent thereto, upon application of compressive force to container 16. Thus, container 16, as illustrated in FIG. 3, is fixedly positioned and extends transverse a leading edge of laminate 13 with its longitudinal marginal seal 36 directed toward the interface between image-receiving layer 18 and auxiliary layer 53. As shown in FIGS. 2 and 3, container 16 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 noted, the image-receiving layer 18 may be temporarily laminated to the next adjacent layer in such a manner that these layers may be separated by the processing composition and relaminated thereby. Procedures for fabricating such prelaminated film units are set forth in the copending applications of A. J. Bachelder and F. J. Binda, Ser. No. 744,912 filed July 15, 1968 and of Edwin H. Land, Ser. No. 804,942 filed Mar. 6, 1969.

In FIG. 6 there is shown a modification of the film unit shown in FIG. 1, wherein the photosensitive element 30a includes a colorless layer 60 coated over the silver halide emulsion and containing one or more precursors of optical filter agents, e.g., pH-sensitive dyes coated at a pH at which they are essentially colorless and thus do not absorb light actinic to said silver halide during photoexposure. Rupture of the pod 16 distributes a pigmented alkaline processing composition effective to raise the pH of said pH-sensitive dye (dyes) and render it (them) light-absorbing, thus providing the desired opaque layer in situ. In addition, solidification of the distributed pigmented processing composition provides a reflecting layer 17b (as shown in FIG. 1) against which the transfer image formed in the image-receiving layer 18 may be viewed through the transparent support 24. In the embodiment shown in FIG. 6 it is usually not necessary to decolorize the alkali-activated optical filter agent if it is nondiffusible to the image-receiving layer (or to a layer through which the transfer image is viewed) and the pigmented reflecting layer 17b is effective to mask it from detracting from the transfer image. Accordingly, the polymeric acid layer 22 may be omitted unless desired for its role in the photographic process, e.g., to reduce the process pH to a level at which development and transfer of image-forming components is terminated and/or to reduce the pH to a level more favorable for image stability and/or to remove from the image layer and immobilize residual reagents potentially harmful to the image.

A variation of the film unit depicted in FIG. 6 is shown in FIG. 7, wherein the colorless layer 60 containing optical filter

agent precursor(s) is coated over the image-receiving layer 18. In this embodiment, it is necessary that the process generated color of the filter agent be discharged to permit the transfer image to be viewed against the reflecting layer without interference. The polymeric acid layer 22 is utilized to effect this color discharge.

Suitable optical filter agents for use in embodiments such as those shown in FIGS. 6 and 7 include the pH-sensitive dyes hereinafter set forth and containing long-chain substituents or "anchors," e.g., alkyl groups containing 10 or more carbons. Suitable precautions should be exercised to avoid desensitization by the optical filter agent precursors, and one such precaution is to immobilize by suitable substituents. Alternatively, selective mordanting may be utilized to avoid undesired diffusion during preuse storage.

The use of long-chain substituents may also be desirable with optical filter agents initially present in the processing composition in order to minimize diffusion from the processing layer into one or more layers of the film unit and consequent reduction of the local concentration of the optical filter agent, thus reducing the light-absorbing effectiveness of a given quantity of the optical filter agent and possible introducing an undesired background color to the final image. Retention of the optical filter agent within the layer containing a reflecting agent, e.g., titanium dioxide, has also been found to give a "multiplication" effect on apparent density, as hereinafter discussed.

A further modification of the embodiment of FIG. 1 is shown in FIG. 8 wherein the image-receiving element 32b includes a preformed reflecting layer 62, e.g., a layer of titanium dioxide, coated over the image-receiving layer 18, photoexposure being effected through this preformed reflecting layer. The opaque processing composition includes one or more optical filter agents to provide an opaque layer 17a, and may also contain a light-reflecting pigment which is the same or different from that in the preformed reflecting layer 62, thus reinforcing the masking capability of the reflecting layer 62. In this embodiment, as in that of FIG. 6, it may not be necessary to decolorize the optical filter agent. Alternatively, the preformed pigmented layer 62 may be coated over the silver halide emulsion 14, in which event (as in the embodiment of FIG. 7) it is necessary to discharge the color of the optical filter agent. The provision of a preformed processing composition permeable layer, intermediate the image-receiving layer and the next adjacent silver halide layer, containing a light-reflecting pigment in a concentration which prior to photoexposure is insufficient to prevent transmission therethrough of exposing actinic radiation and which, subsequent to processing, possesses a covering and reflecting capacity effective to mask the developed silver halide emulsion layer(s) and associated residual image-forming material is described in detail in the copending applications of Edwin H. Land, Ser. No. 846,441 filed July 31, 1969 (now U.S. Pat. No. 3,615,421 issued Oct. 26, 1971 and of Sheldon A. Buckler, Ser. No. 3,646 filed Jan. 19, 1970.

FIG. 9 illustrates yet another modification (of the embodiment shown in FIG. 1) wherein the polymeric acid layer 22 and the spacer layer 20 are positioned in the photosensitive element 30b between the opaque support 10 and the dye developer layer 12. If desired, additional alkali neutralizing capability may be provided by replacing the image-receiving element 32c which does not contain a polymeric acid layer with a receiving sheet 32 which does contain such a polymeric acid layer.

In FIG. 10 there is shown an embodiment of this invention in the formation of silver transfer prints. Photosensitive element 130 comprises an opaque support 10 carrying a silver halide emulsion 14. An image-receiving element 132 comprising a transparent support 24 carrying, in turn, a polymeric acid layer 22, a spacer layer 20 and a silver receptive stratum 118, is positioned in superposed relationship with the photosensitive element 130 with a rupturable pod 16 positioned to distribute an opaque processing composition 117

between the superposed elements. In accordance with the well-known details of silver transfer processes, exposed silver halide is reduced in the photosensitive layer and a soluble, diffusible complex is formed with unexposed and underdeveloped silver halide. This soluble complex is transferred to the silver-receptive stratum 118 which preferably contains one or more silver-precipitating agents or nuclei. After the process has proceeded to the point wherein exposure of the silver halide emulsion 14 is no longer detrimental, the pH of the applied processing composition layer is reduced by the polymeric acid, in a manner analogous to that described in connection with FIG. 1, and the optical filter agent which rendered the processing composition opaque is rendered colorless. The silver transfer image in the silver-receptive stratum 118 may be viewed through the transparent support 24 against a reflecting layer provided by white pigment dispersed in the layer resulting from solidification of the applied processing composition.

In the embodiments heretofore described, the desired image has been viewed against a reflecting layer, i.e., the final image is a reflection print. This invention is also applicable to the formation of images viewed by transmitted light. One such embodiment by which a developed and stabilized negative may be obtained (without concurrent formation of a transfer image) is shown in FIG. 11 wherein a first or photosensitive element 230 comprises a transparent support 24 carrying a colorless layer 60 containing an alkali-activated optical filter agent (or a preformed alkali-dischargeable dye) and a layer 14 of a silver halide emulsion. A second element 232 in superposed relationship with the photosensitive element 230 (and prelaminated thereto as discussed above, if so desired) comprises a transparent support 24 carrying a polymeric acid layer 22 and a timing layer 120. A rupturable pod 16 containing an opaque processing composition 117a is so positioned as to distribute said processing composition between the silver halide emulsion 14 and the timing layer 120. Permeation of alkali from the processing composition activates the optical filter agent (layer 60) thus providing protection for the developing silver halide emulsion 14 from light incident upon the transparent support 24. The timing layer 120, like the spacer layer 20 in previously discussed embodiments, is of a thickness and polymeric composition effective to control the permeation of alkali therethrough to the polymeric acid layer 22, thus determining when the pH is reduced to a level rendering essentially colorless the optical filter agents in the processing composition and in the light barrier layer 60 behind the silver halide emulsion 14. (Since the image formed in the embodiment of FIG. 11 is to be viewed by transmitted light, it is not essential that the optical filter agent layers shielding the silver halide emulsion become completely colorless so long as these layers become substantially light transmitting, i.e., the optical filter agent may retain some coloration. The processing composition 117a released by the rupture of pod 16 is free of reflecting pigment which would interfere with viewing the final image by transmitted light. (If desired, however, a reflecting pigment could be included in the processing composition 117a and the final image viewed by reflected light.) One process by which stabilized silver negative images may be prepared and which may be used in the embodiment of FIG. 11 is described in the copending application of Edwin H. Land, Ser. No. 888,919 filed Dec. 29, 1969. As disclosed therein, an element suitable for use as the polymeric acid containing element 232 in FIG. 11 may be prepared by applying to the subcoated surface of a cellulose triacetate sheet an aqueous solution comprising 70 parts by weight of poly(ethylene/maleic anhydride) commercially available from Monsanto Chemical Co. as "DX Resin Grade 840-11-03" and parts by weight of "Elvanol 70-05" (trademark of E. I. duPont de Nemours and Co. for a low-viscosity, completely hydrolyzed polyvinyl alcohol) to provide a polymeric acid layer about 0.4 mil. thick. A timing layer about 0.15 mil. thick may then be applied comprising a graft copolymer of diacetone acrylamide and acrylamide on polyvinyl alcohol prepared in the manner described in the copend-

ing application of Lloyd D. Taylor, Ser. No. 790,747, filed Jan. 13, 1969 (now U.S. Pat. No. 3,575,701 issued Apr. 20, 1971). A suitable processing composition for use in this embodiment may comprise (in addition to a pH-sensitive dye):

Water	902.0 cc.
Hydroxyethyl cellulose	41.5 g.
Sodium sulfite	33.0 g.
Potassium thiosulfate	14.0 g.
Ascorbic acid	60.0 g.
2,4-diamino-orthocresol	2.0 g.
cysteine	2.2 g.
diethylamine	50.0 cc.
Sodium hydroxide	25.0 g.

which has been found effective to develop exposed silver halide and to form a stable complex with unexposed silver halide, as disclosed in U.S. Pat. No. 3,343,958 to which reference may be made. Other procedures known in the art to provide developed and fixed silver images may also be used. It will be understood that "positive" developed and fixed (stabilized) silver images may be obtained in accordance with the embodiment of FIG. 11 by using one of the so-called direct positive silver halide emulsions, including internal latent image emulsions; such silver halide materials and compositions for developing them are well known in the art and need not be described in detail here.

Film units constructed in accordance with FIG. 11 may be exposed through either transparent support 24. If desired, the colorless layer 60 containing an alkali-activated optical filter agent may be replaced by a layer containing an optical filter agent in a light-absorbing state as coated which will also serve as an antihalation layer; pH reduction may be used to discharge the resulting light barrier layer. Also, if desired or necessary, a second polymeric acid layer 22 and timing layer 22 may be positioned in the photosensitive element to insure sufficient neutralizing capability and a more uniform pH throughout the laminate and thus provide more even discharge of the optical filter agent color. In lieu of providing the optical filter agent (whether colored or latent in a layer of the photosensitive element 230, the desired opaque layer may be provided by distributing a second opaque fluid between appropriate strata of the photosensitive element; this second opaque fluid may include some or no photographically active components, and the stratum provided by solidification of the film-forming polymer dissolved therein remains as part of the laminate, the color of the optical filter agent being discharged.

FIG. 12 illustrates the application of this invention to diffusion transfer processes providing additive color images. As shown therein, an additive color photosensitive element 234 comprises a transparent support 24 carrying, in turn, an additive color screen 119 ("R," "B" and "G" representing, respectively, red, blue and green segments of an additive color screen), a silver-receptive stratum 118, a colorless layer 60 containing an alkali-activated optical filter agent, and a silver halide emulsion layer 14. A second element 232 as described in connection with FIG. 11 is positioned in superposed relationship with said photosensitive element 234 with a rupturable pod 16 containing an opaque processing composition 117 positioned to release said processing composition between said timing layer 120 and said silver halide emulsion layer 14. Application of the processing composition renders the optical filter agent colored, thereby providing light opacity for the developing silver halide emulsion with respect to light incident upon either transparent support 24. Unexposed silver halide is dissolved and transferred to the silver-receptive stratum 118 where it is deposited in a high covering power silver image. The exposed silver halide is developed to provide a low covering power silver image in the silver halide emulsion layer 14. These two silver images when viewed by transmitted light appear as a positive image and are so used in combination with the additive color screen 119 to provide the desired additive color transparency. After an appropriate time interval, sufficient alkali is neutralized by the polymeric acid layer 22 to

reduce the pH to a level effective to decolorize the optical filter agents of the processing composition and of the optical barrier layer 60.

If desired, the separate silver-receptive stratum 118 may be omitted and the requisite silver-precipitating nuclei incorporated into the silver halide emulsion layer 14. The formation of additive color images using silver halide emulsions containing silver precipitants is described in U.S. Pat. No. 3,536,488 issued to Edwin H. Land on Oct. 27, 1970.

It will be recognized that light incident upon the exposure surface of certain embodiments of this invention, e.g., of transparent support 24 of the embodiment shown in FIG. 12, may pass through all of the layers of photosensitive element 234 and second element 232. If the film unit is part of a film pack containing a plurality of such film units, the light so transmitted could effect a photoexposure of at least the next underlying unit. This problem may be readily avoided by interposing an opaque member between the stacked film units. Such an opaque member may be a separate opaque interleaf sheet positioned between film units, or it may be an opaque layer so secured to the outer surface of the transparent support 24 of the second element, e.g., by a peelable or other temporary adhesive layer, as to be readily removed after processing. Still another technique for accomplishing such protection against premature exposure of underlying film units is to provide an alkali-bleachable dye, e.g., of the antihalation type, of appropriate density in layer 120 of FIG. 12; this density need not be very great since their exposure time is very short.

FIG. 13 illustrates an embodiment of this invention wherein the desired image is obtained by silver-catalyzed bleaching of a dye, the unbleached dye providing the desired visible image. As shown therein, a film unit comprises a photosensitive element 230 in superposed relationship with an image-receiving element 236 with a rupturable pod 16 positioned to release an opaque processing composition between said superposed elements. The photosensitive element 230 comprises a transparent support 24 carrying a colorless layer 60a containing an alkali-activated optical filter agent and a silver halide emulsion layer 14. The image-receiving element 236 comprises a transparent support 24 carrying, in turn, a polymeric acid layer 22, a spacer or timing layer 20 and a silver-receptive stratum 218 containing a bleachable dye, e.g., an azo dye bleachable in the presence of metallic silver. Application of the processing composition 117 results in the formation of an opaque layer, from the alkali-activated optical filter agent, development of the exposed silver halide emulsion, and formation of a silver transfer image in the silver-receptive stratum 218. Alkali neutralization after transfer image formation reduces the pH to a level which discharges at least the optical filter agent contained in the opaque processing composition and activates a bleach agent, thereby bleaching imagewise the nondiffusible dye initially present in the silver receptive stratum. The unbleached dye provides a negative image. If the opaque processing composition includes a reflecting pigment, the negative dye image may be viewed by reflection against the resulting reflecting layer, e.g., such as the white pigmented layer 17b of FIG. 1, and it is not necessary to discharge the color generated by the optical filter agent (layer 60a). Alternatively, the opaque processing composition 117 may be free of white pigment in which event the color in both opaque strata is discharged and the dye image viewed by transmitted light. If the dye in the silver-receptive stratum 218 is a color-shifted dye, e.g., a dye containing an esterified auxochrome, it may be colorless prior to contact with alkali and photoexposure thus made through that layer. Silver dye bleach procedures are well known in the art, e.g., U.S. Pat. No. 3,414,411 and need not be described in detail here.

It will be recognized that layer 60 containing an alkali-activated optical filter agent may be omitted in embodiments such as those illustrated in FIGS. 11 and 12 if an optical filter agent initially present in the processing composition is diffused into and throughout the silver halide emulsion layer and

retained therein so as to protect unexposed silver halide from post exposure fog.

FIG. 18 illustrates another film structure embodying this invention. In this embodiment, a photosensitive element 134 comprises a transparent support 24 carrying a layer 22 of a polymeric acid, a spacer layer 20, an image-receiving layer 18, an opaque layer 62, a dye developer layer 12, a silver halide emulsion layer 14, and a colorless layer 60 containing an alkali-activated optical filter agent. After photoexposure, a processing composition 17 is applied by rupturing pod 16 and distributing the processing composition between a cover or spreader sheet 64 and layer 60. The cover sheet 64 may be transparent, in which event photoexposure may be effected through it and it may be secured to photosensitive element 134, e.g., by a binder tape around the edges of the film unit or by temporary lamination as discussed above, prior to photoexposure. Alternatively, cover sheet 64 may be opaque in which event it is positioned out of the exposure path prior to photoexposure, as described in connection with the image-receiving element in the embodiment illustrated in FIG. 5. The processing composition may contain a white pigment, e.g., titanium dioxide, where cover sheet 64 is transparent and it is desired to provide a "white back" for the final laminate. Where opacifying capability additional to that provided by layer 60 is desired, the processing composition may contain suitable opacifying agents, e.g., carbon black, titanium dioxide, etc. Opaque layer 62 includes a white pigment, such as titanium dioxide, to provide a white background against which the transfer image may be viewed. If desired, additional opacification may be provided by adding a small amount of carbon black to the opaque layer 62, or by providing a layer of carbon black between the dye developer layer 12 and the opaque layer 62 containing, e.g., titanium dioxide. While the embodiment shown in FIG. 18 has been directed to the formation of dye images using, e.g., dye developers, it will be readily apparent that similar techniques may be used in the formation of silver transfer images.

A number of modifications to the structures described in connection with the figures will readily suggest themselves to one skilled in the art. Thus, for example, the multicolor multilayer negative shown in FIGS. 3 and 4 may be replaced by a screen-type negative as illustrated in U.S. Pat. No. 2,968,554 issued Jan. 17, 1961 to Edwin H. Land and in the aforementioned U.S. Pat. No. 2,983,606 particularly with respect to FIG. 3 thereof. Similarly, dye developers may be replaced by color-providing substances reducible by unreacted silver halide developing agent in accordance with the teachings of U.S. Pat. No. 3,185,567 issued May 25, 1965 to Howard G. Rogers.

While many of the color-providing substances discussed above are initially diffusible in the appropriate processing composition, it should be understood that one may also use a compound which is initially nondiffusible in the particular photographic reagent employed for development but which can provide by appropriate chemical reaction an imagewise distribution of a mobile and diffusible color-providing moiety which may then be transferred, at least in part, by diffusion to an image-receiving layer or dyeable stratum to impart thereto a color transfer image. As examples of nondiffusible compounds of this description, mention may be made of those compounds containing a diffusible color-provided moiety which may be a complete dye or a dye intermediate, e.g., a coupler, and an "anchoring" moiety rendering the compound nondiffusible. Upon appropriate chemical reaction, e.g., oxidation, coupling, etc., the color-providing moiety is separated from the anchoring moiety and is thus free for transfer to the dyeable stratum to form the desired color transfer image.

One such class of these compounds are those disclosed, for example, in U.S. Pat. Nos. 3,443,940 issued to Stanley M. Bloom and Howard G. Rogers and 3,443,939 issued to Stanley M. Bloom and Robert K. Stephens. These compounds may be defined as nondiffusible compounds containing a diffusible color-providing moiety, which compounds are capable of providing, as a function of development of an exposed light-

sensitive silver halide layer, a reaction product which can autoreact intramolecularly to effect ring closure and as a result thereof, to split off a mobile and diffusible moiety which may be colored and used as an image-forming material.

Other nondiffusible compounds and reaction mechanisms employing the same include, for example, the compounds and systems employing them to obtain color transfer images which are disclosed in U.S. Pat. Nos. 3,227,550; 3,227,551; 3,227,552; 3,227,554; 3,243,294; and 3,445,228. In general, these aforementioned patents relate to systems employing a nondiffusible coupler which can couple with the oxidation product of an aromatic primary amino color developing agent to provide a diffusible dye which may be transferred by diffusion to a dyeable stratum to impart thereto either a positive or a negative transfer image, depending upon the particular system employed.

The various techniques described in the above-noted patents for forming either negative or positive images may be readily adapted for processing outside a camera by application of the principles of the present invention.

In the preferred embodiment of this invention, the film unit is specifically adapted to provide for the production of a multicolor dye transfer image and the photosensitive laminate comprises, in order of essential layers, a dimensionally stable opaque support layer; at least two selectively sensitized silver halide emulsion strata each having dye image-providing materials of predetermined color associated therewith which are soluble and diffusible, in alkali, at a first pH; the alkaline solution permeable polymeric layer dyeable by the dye image-providing materials; the alkaline solution permeable polymeric acid layer containing sufficient acidifying groups to effect reduction, subsequent to substantial multicolor transfer dye image formation, of a processing composition having the first pH to a second pH, at which the dye image-providing material is insoluble and nondiffusible and to effect the discharge of the optical filter agent's color and a dimensionally stable transparent layer.

The silver halide emulsions comprising the multicolor photosensitive laminate preferably possess predominant spectral sensitivity to separate regions of the spectrum and each has associated therewith a dye, which is a silver halide developing agent and is, most preferably, substantially soluble in the reduced form only at the first pH, possessing a spectral absorption range substantially complementary to the predominant sensitivity range of its associated emulsion.

In the preferred embodiment, each of the emulsion strata, and its associated dye, is separated from the remaining emulsion strata, and their associated dye, by separate alkaline solution permeable polymeric interlayers and the dyeable polymeric layer is separated from the polymeric acid layer by an alkaline solution permeable polymeric spacer layer, most preferably a polymeric spacer layer having decreasing permeability to alkaline solution with increasing temperature.

In such preferred embodiment, the silver halide emulsion comprises photosensitive silver halide dispersed in gelatin and is about 0.6 to 6 microns in thickness; the dye itself is dispersed in an aqueous alkaline solution polymeric binder, preferably gelatin, as a separate layer about 1 to 7 microns in thickness; the alkaline solution permeable polymeric interlayers, preferably gelatin, are about 1 to 5 microns in thickness; the alkaline solution permeable and dyeable polymeric layer is transparent and about 0.25 to 0.4 mil. in thickness; the alkaline solution permeable polymeric spacer layer intermediate the dyeable polymeric layer and the polymeric acid layer is transparent and about 0.1 to 0.7 mil. in thickness; the alkaline solution permeable polymeric acid layer is transparent and about 0.3 to 1.5 mil. in thickness; and each of the dimensionally stable opaque and transparent supports are alkaline solution impermeable and about 2 to 6 mil. in thickness. It will be specifically recognized that the relative dimensions recited above may be appropriately modified, in accordance with the skill of the art and the process being performed.

Such film unit should also include a rupturable container, retaining an alkaline processing solution having the first pH and containing dispersed therein a reflecting agent in a quantity sufficient to mask the developed photosensitive layers and untransferred dyes fixedly positioned and extending transverse a leading edge of the photosensitive element so as to effect unidirectional discharge of the container's contents between the dyeable polymeric layer and the silver halide emulsion layer next adjacent.

The respective layers comprising the composite structure are secured in fixed relationship which, in whole or in part, may be readily and simply achieved by retaining means such as, for example, a pressure-sensitive tape binding member extending around the edges of the composite structure securing or maintaining the layers of the composite together at their respective edges.

In a preferred embodiment of the present invention's film unit for the production of a multicolor transfer image, the respective plurality of silver halide/dye developer units of the composite structure are predominantly responsive to separate regions of the spectrum and provide a chromatic image possessing an absorption range substantially complementary to the sensitivity range. In general, the composite structure will most preferably be in the form of a multilayer configuration which will ordinarily comprise a cyan dye developer/red-sensitive emulsion unit contiguous the stable opaque layer, a yellow dye developer/blue-sensitive emulsion unit most distant from the opaque layer and a magenta dye developer/green-sensitive emulsion unit between the preceding units, recognizing that the relative relationship of such units may be varied in accordance with the desires of the operator. It will also be recognized that the dimensionally stable polymeric support layer next adjacent the photosensitive silver halide emulsion layer or layers may be transparent, as disclosed in U.S. Pat. No. 3,415,646 issued Dec. 10, 1968 to Edwin H. Land, and that in such instance the opacifying agent may be initially dispersed in the composite film unit intermediate the dyeable polymeric layer and the silver halide emulsion layer next adjacent, as disclosed in U.S. Pat. No. 3,415,645 issued Dec. 10, 1968 to Edwin H. Land.

The structural integrity of the composite structure may be maintained, at least in part, by the adhesive capacity exhibited between the various layers comprising the structure at their opposed surfaces. However, the adhesive capacity exhibited at an interface intermediate image-receiving layer and the silver halide emulsion layer next adjacent thereto, for example, intermediate image-receiving layer and the blue-sensitive silver halide emulsion layer, should be less than that exhibited at the interface between the opposed surfaces of the remainder of the layers forming the structure, most preferably, on the order of substantially no adhesion, in order to facilitate distribution of processing solution intermediate the image-receiving layer and the silver halide emulsion layer next adjacent thereto. The composite'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 the composite structure, and maintaining the layers comprising the structure intact, except at the above-noted interface during distribution of the alkaline solution intermediate those layers. The binding member may comprise a pressure-sensitive tape securing and or maintaining the layers of the structure together at its respective edges. If the edge binder tapes are also opaque, edge leakage of actinic radiation incident on the emulsion or emulsions will also be prevented. The selected light-reflecting agent, however, 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 such agent may be employed, it is preferred that an 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 light-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 thereof, mention may be made of barium sulfate, zinc oxide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

A particularly preferred agent comprises titanium dioxide due to its highly effective reflection properties. In general, based upon percent titanium dioxide ("weight volume"), a processing composition containing about 40-50 grams of titanium dioxide suspended in 100 cc. of water will provide a percent reflectance of about 85-90 percent. In the most preferred embodiments, the percent reflectance particularly desired will be in the order of above 85 percent.

Where it is desired to increase the radiation filtering capacity of a processing composition containing a reflecting agent selected predominantly for its radiation-reflecting properties, such as, for example, titanium dioxide, beyond that ordinarily obtained or required to obscure or mask the dye and/or developed silver associated with the photosensitive silver halide emulsion layers, it may also be desirable to provide an additional light-absorptive agent, exhibiting more effective filtration of radiation incident on the transparent support layer during processing, such as carbon black, for example, added in a concentration of about 1 part carbon black to 100 to 500 parts titanium dioxide, in order to further protect the emulsions from fog formation during such processing.

In addition to preformed reflecting agents, it is also within the scope of this invention to employ reflecting agent precursors, e.g., materials capable of forming the requisite agent in situ during processing, as disclosed and claimed in the copending application of Edwin H. Land, Ser. No. 43,742 filed June 5, 1970. As an example of such precursors, mention may be made of ionizable white inorganic visible light-reflecting pigment generating salts such as barium chloride, zirconium chloride and the like, the cation of which upon contact with sulfate ions present in the processing composition and generally derived from ionizable salts such as sodium sulfate, etc., form reflecting agent or pigment salts such as barium sulfate and the like; ionizable salts such as zinc sulfate and the like, the cation of which upon contact with the anion of ionizable sodium or potassium hydroxide present in the processing composition form reflecting agent pigments such as zinc oxide and the like; ionizable salts such as zinc acetate and the like, the cation of which upon contact with sulfide ions present in the processing composition and generally derived from ionizable salts such as sodium sulfide etc., form reflecting agents such as zinc sulfide and the like, etc.

The present invention will be further illustrated by the following example intended to be illustrative only.

EXAMPLE

A photosensitive element was prepared by coating an opaque cellulose triacetate support with a layer of the magenta dye developer 2-(p-[β-hydroquinonyl-ethyl]-phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin at a coverage of 70 mg./ft.² of dye and about 100 mg./ft.² of silver and 60 mg./ft.² of gelatin. A yellow filter dye was coated over this silver halide emulsion effective to absorb blue and short-green wavelength light, so that the green-sensitive silver halide emulsion was exposable essentially only by long-wavelength green light. The photosensitive element was photoexposed and a layer approximately 0.0024 inches thick of a processing composition comprising:

Water	100 cc.
Potassium hydroxide	11.2 g.
Hydroxyethyl cellulose (high viscosity) (commercially available from Hercules Powder Co.,	3.4 g.

23

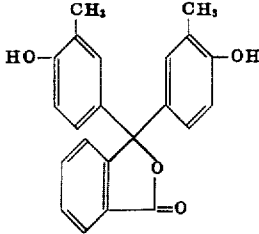
Wilmington, Delaware, under the
trade name Natrasol 250]
N-benzyl- α -picolinium bromide
Benzotriazole
Titanium dioxide
Thymolphthalein

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1.0 g.
50.0 g.
1.7 g.

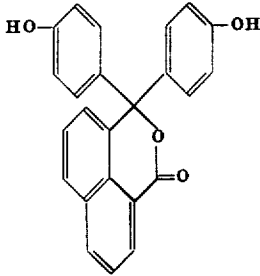
was spread between the exposed photosensitive element and the image-receiving layer at 73° F. The resulting laminate was maintained intact and removed from a dark area within a minute and the transfer image formation was observed through the transparent polyester support. The thymolphthalein has a maximum absorption at 583 μ and thus is effective to absorb "long green" light. After 2 minutes, the titanium dioxide layer (formed by solidification of the layer of processing composition) was visible to the eye in the highlight areas of the transfer image as a white layer, indicating that the polymeric acid had reduced the pH to a level at which the thymolphthalein was essentially colorless. The image-receiving element used was prepared as follows: A transparent polyethylene terephthalate film base was coated, in succession, with a layer of the partial butyl ester of polyethylene/maleic anhydride copolymer to provide a polymeric acid layer approximately 0.00045 inches thick, followed by a spacer layer of polyvinyl alcohol approximately 0.0003 inches thick, followed by an image-receiving layer approximately 0.0002 inches thick comprising a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine and a small amount of 1-phenyl-5-mercaptotetrazole.

Other reagents which may be used as optical filter agents in accordance with this invention include:

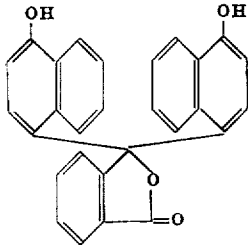
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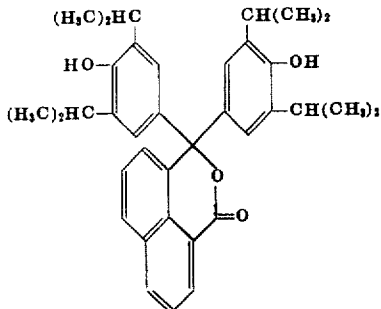
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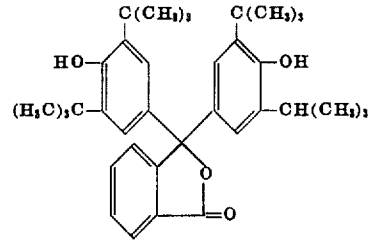


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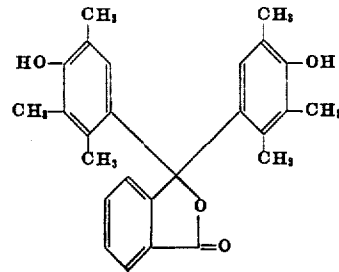


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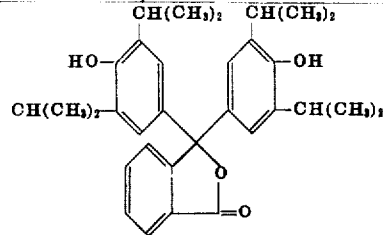
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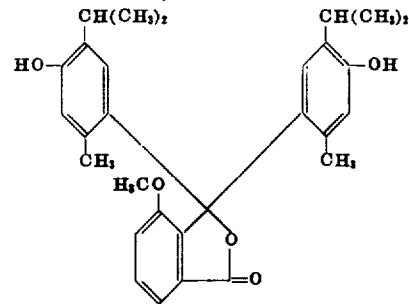
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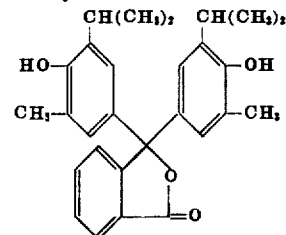
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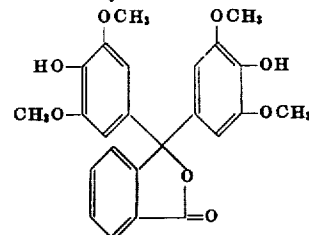
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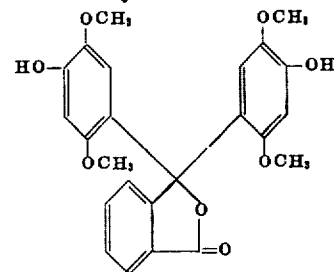
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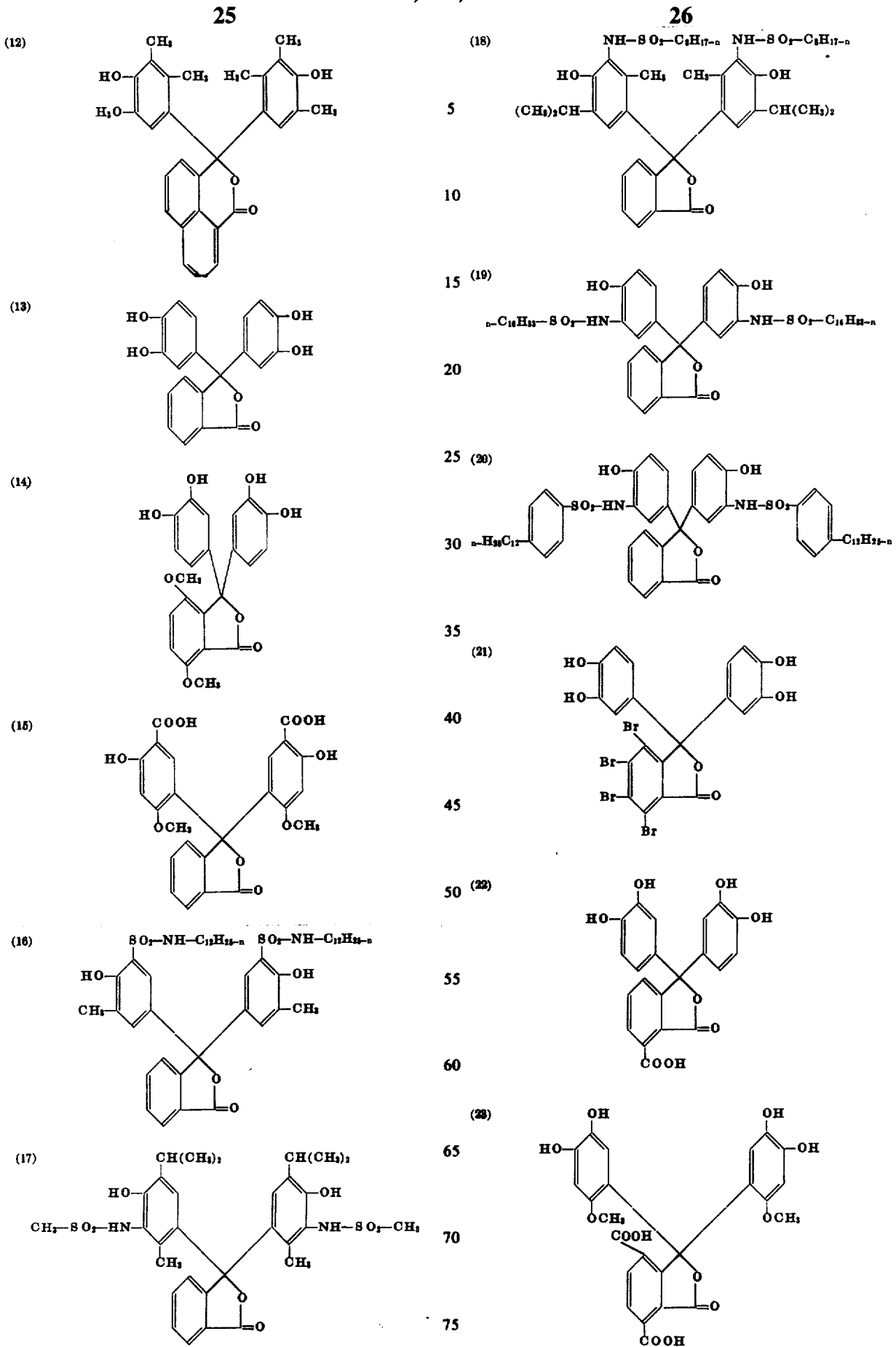


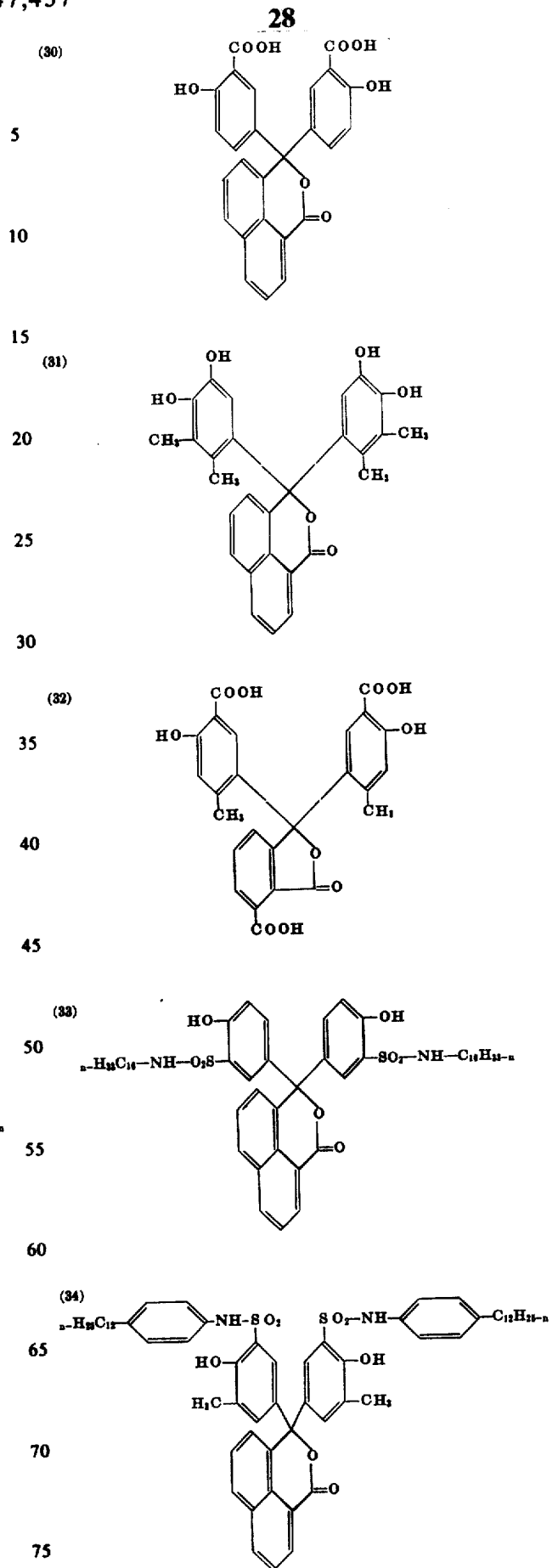
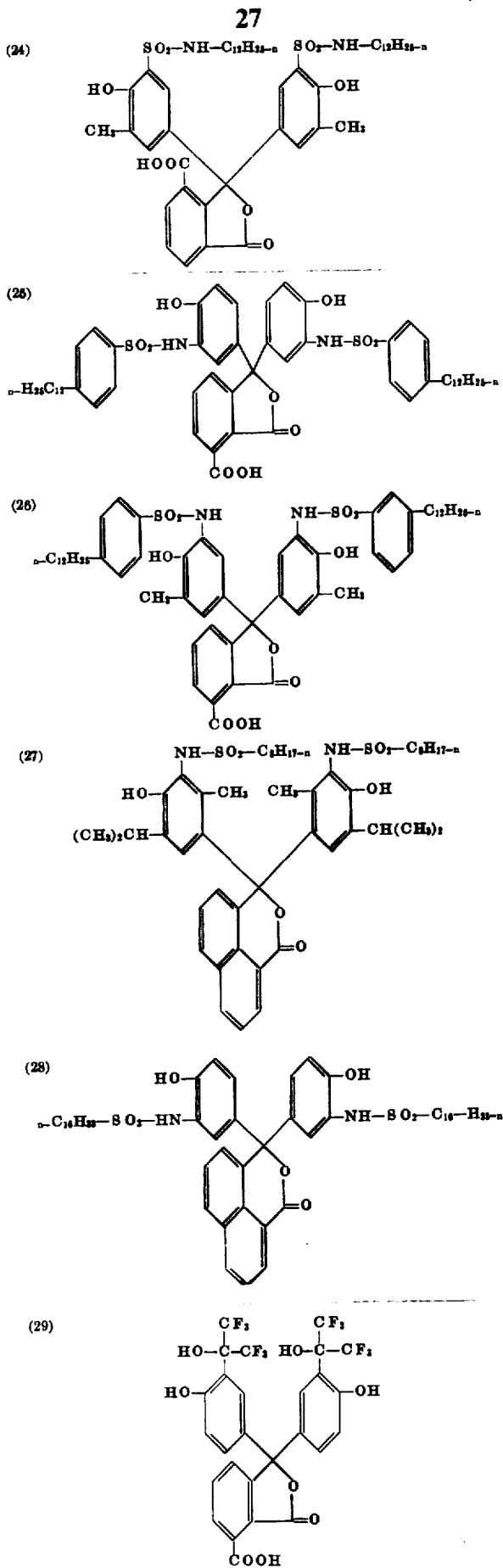
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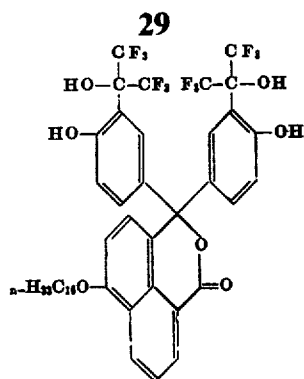
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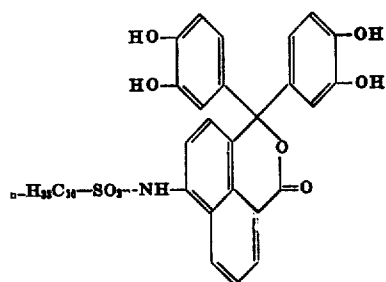




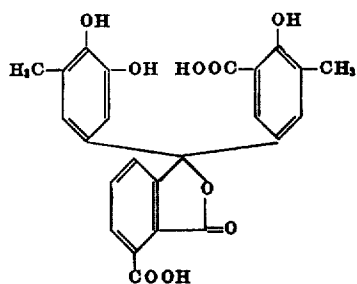
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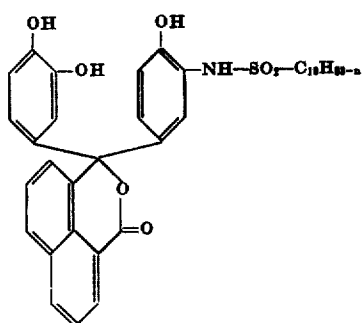
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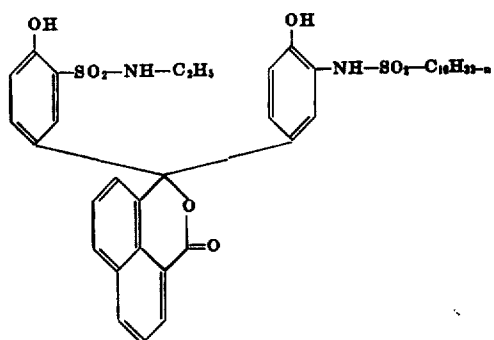
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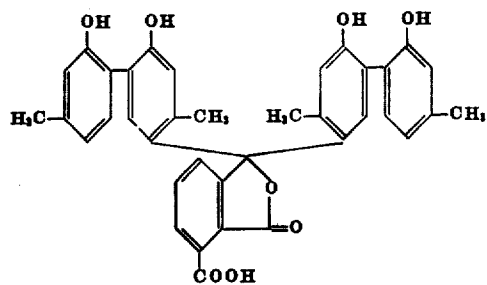
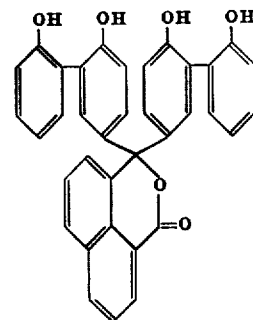
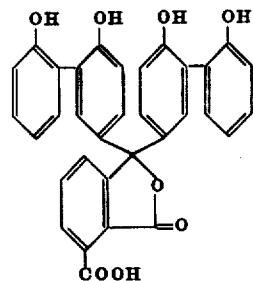
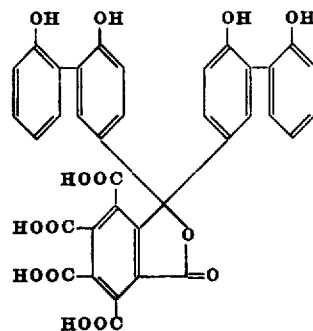
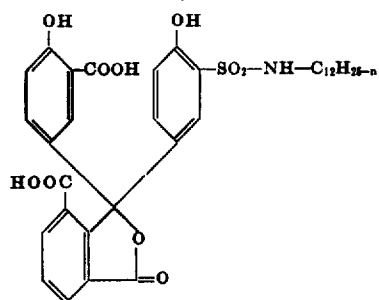
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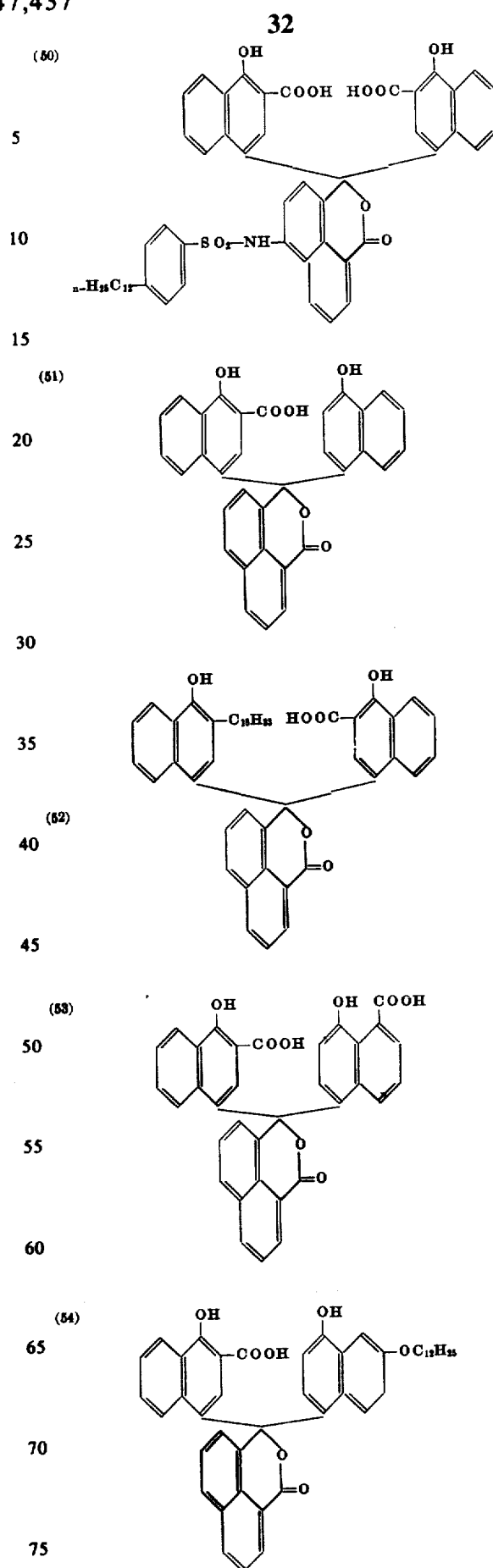
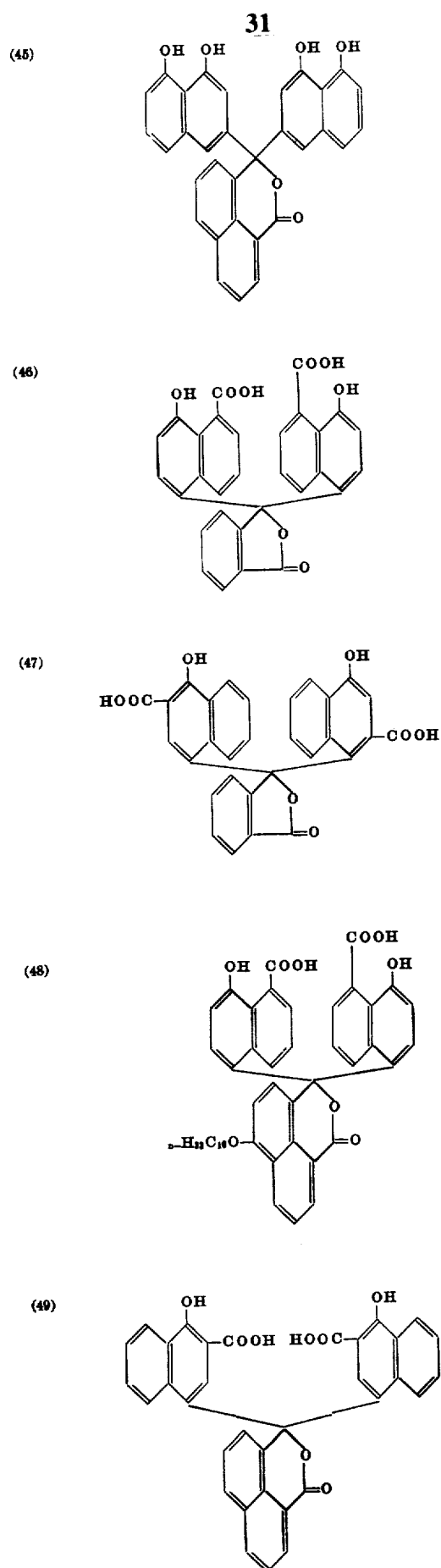
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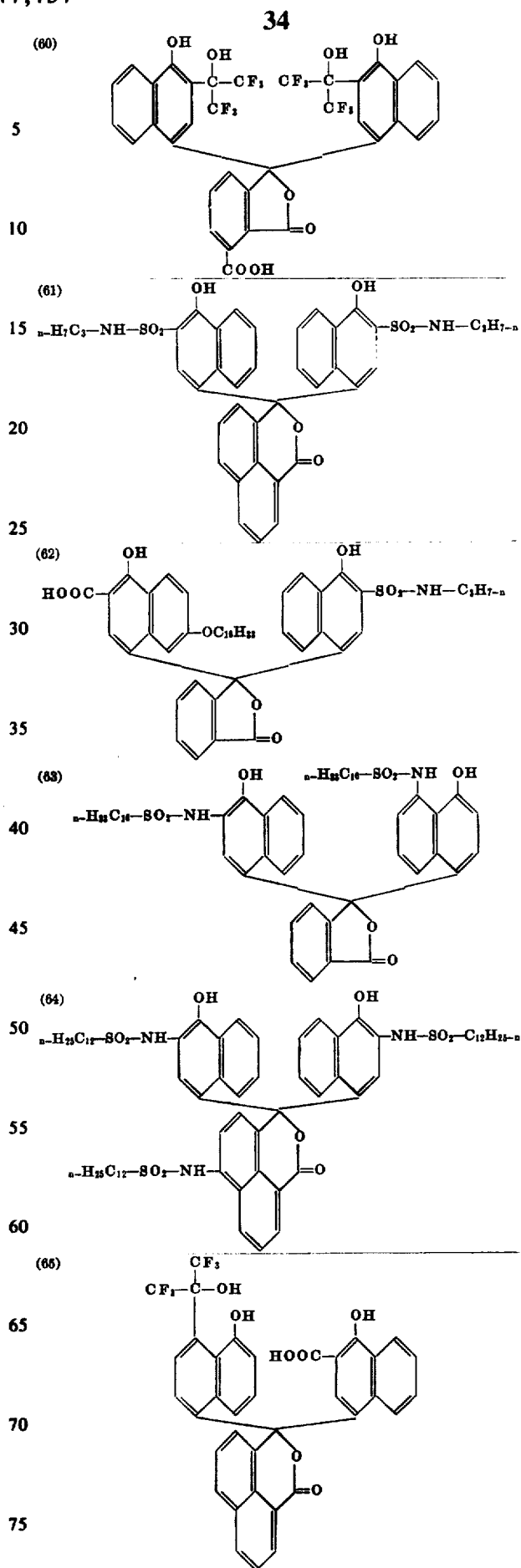
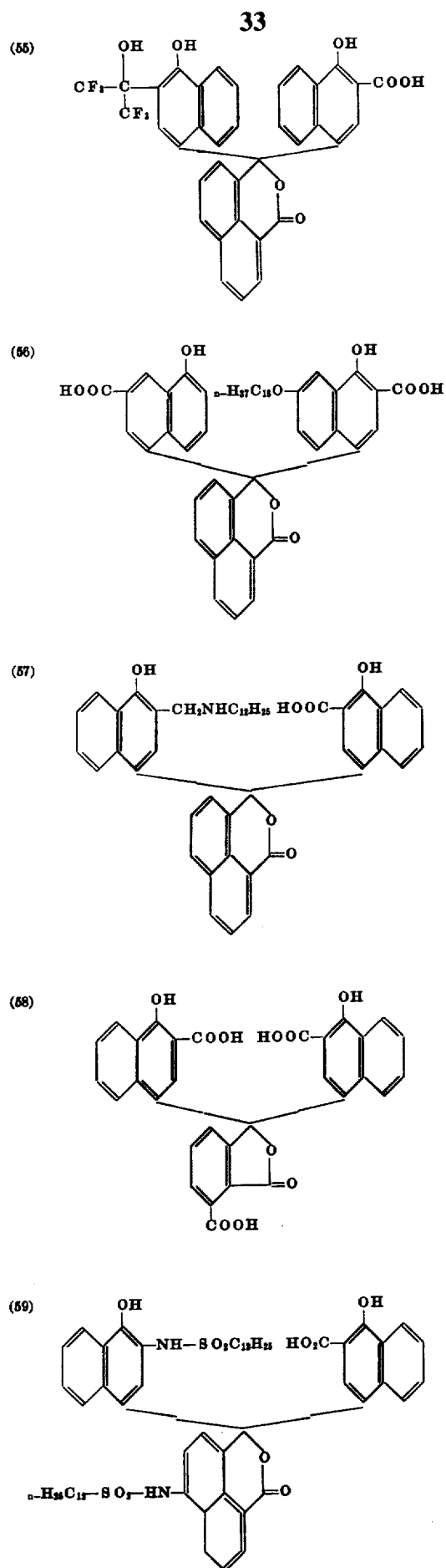
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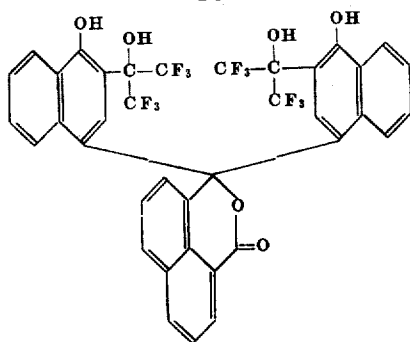
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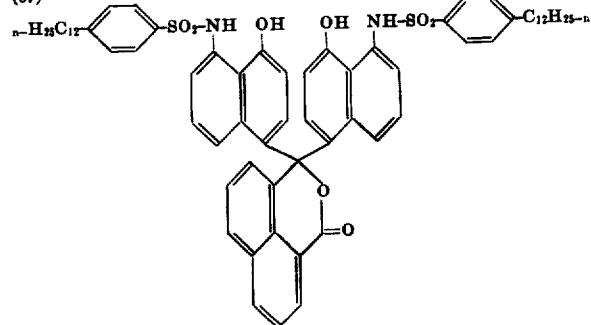
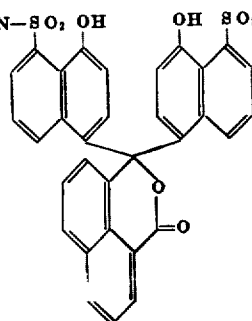


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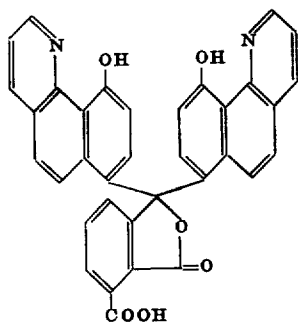
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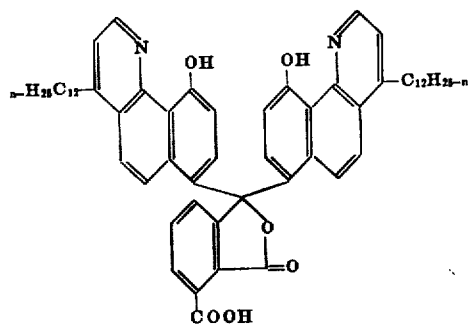
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(68) $n\text{-H}_{25}\text{C}_{14}\text{-HN-SO}_2$ 

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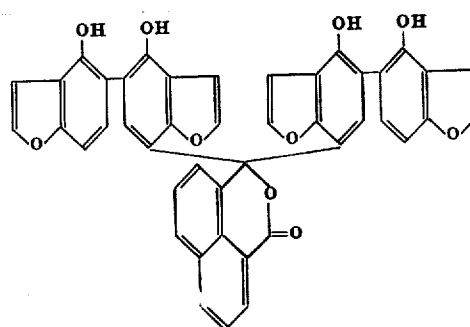
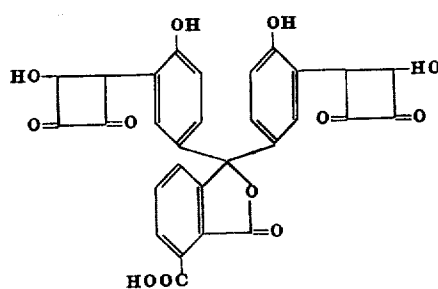
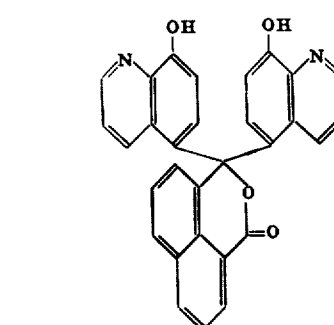
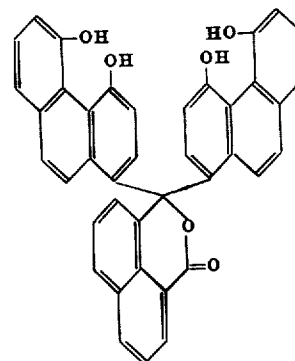
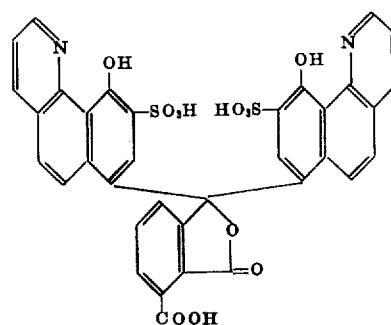
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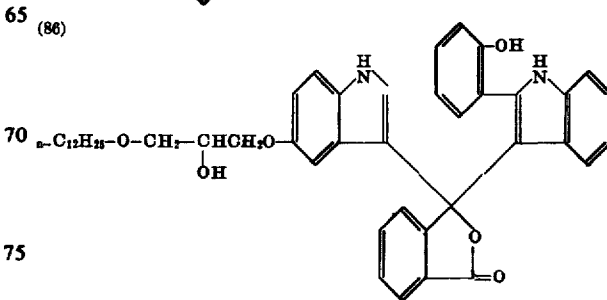
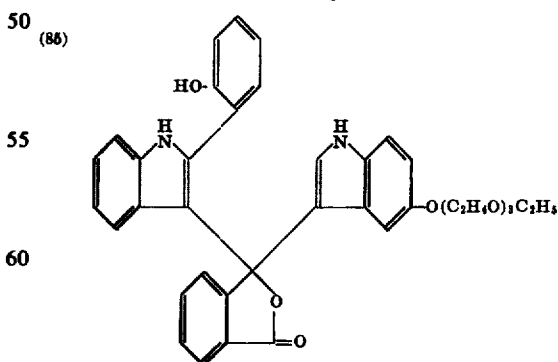
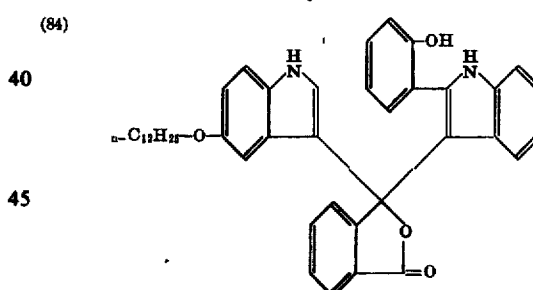
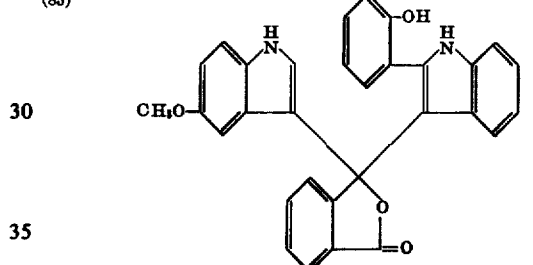
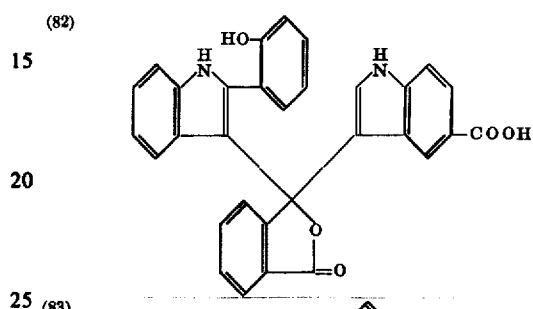
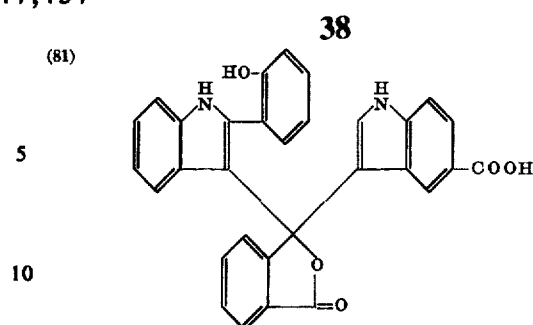
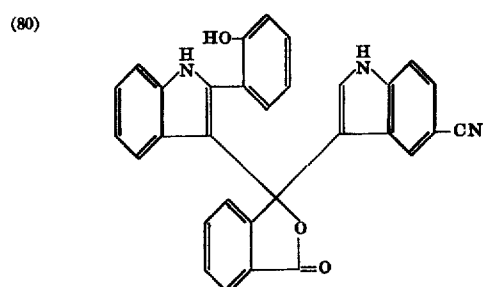
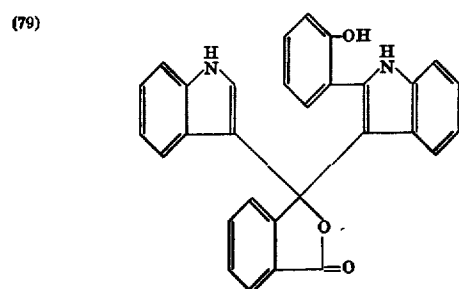
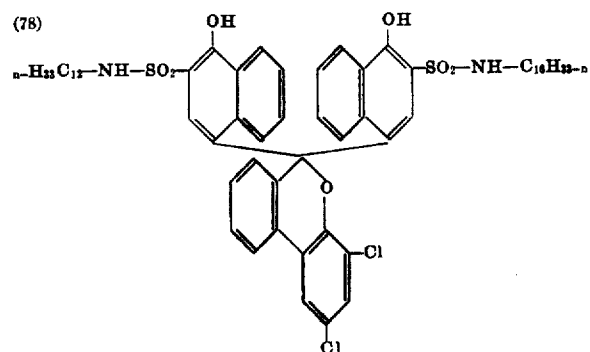
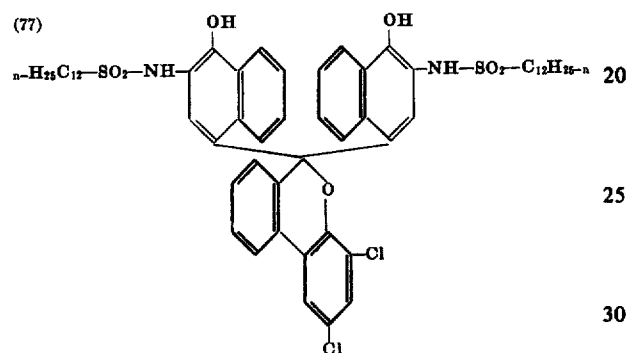
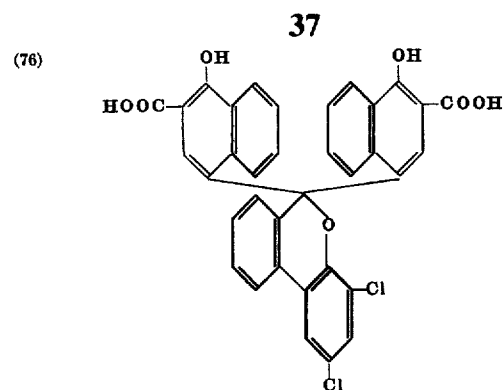
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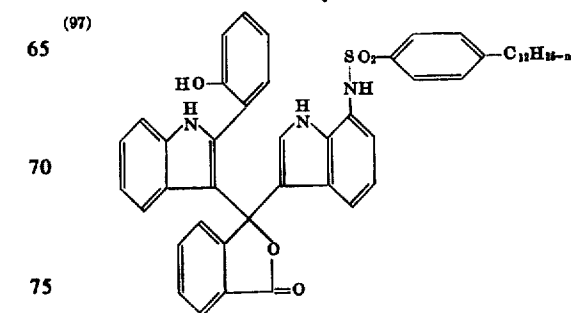
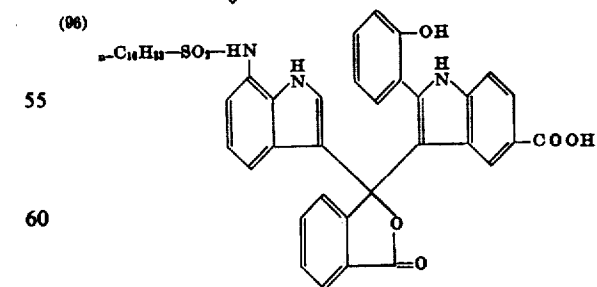
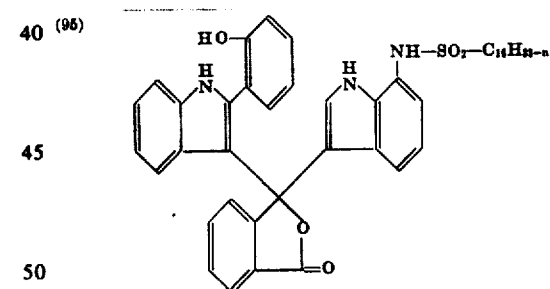
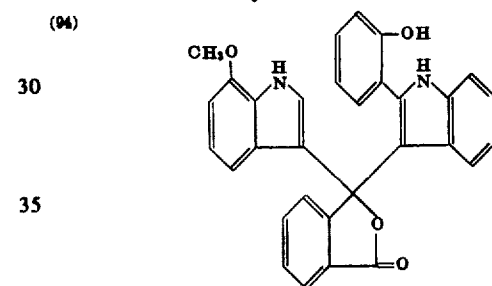
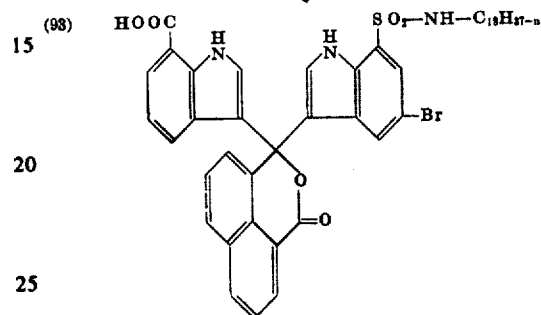
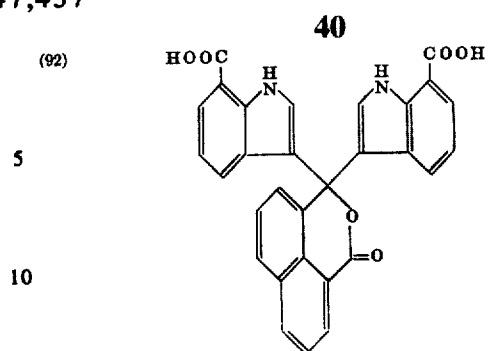
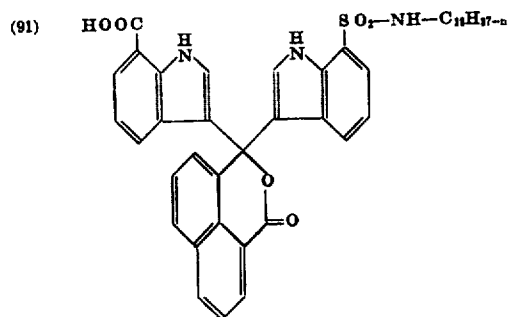
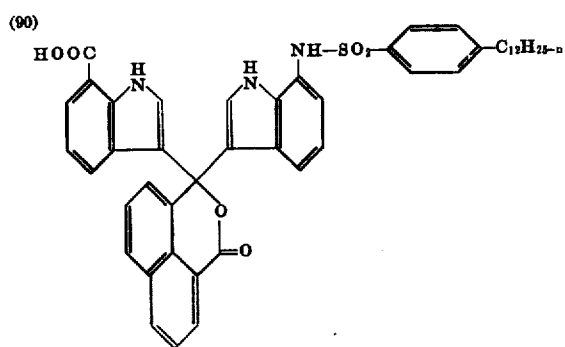
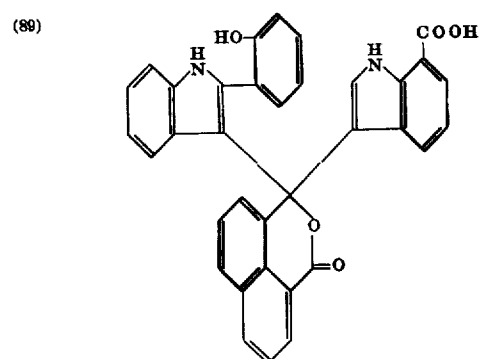
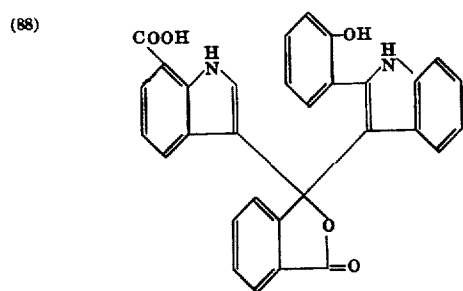
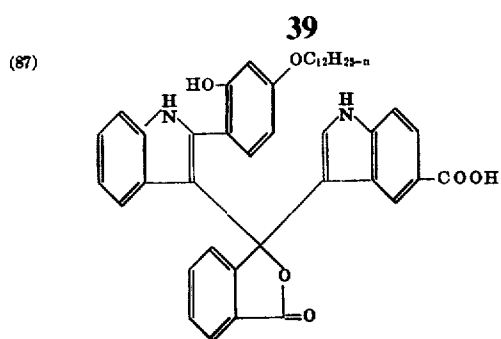
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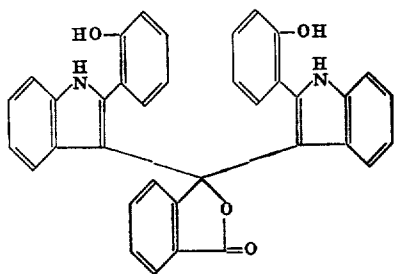




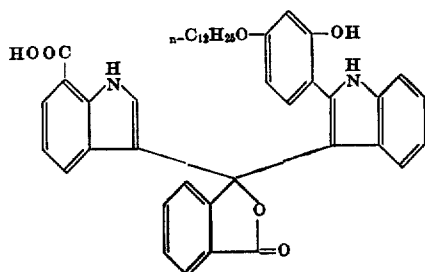


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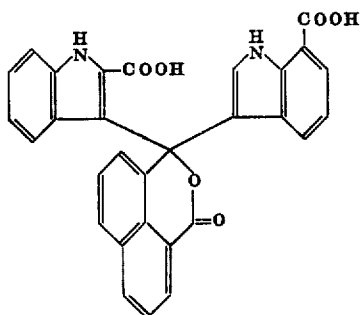
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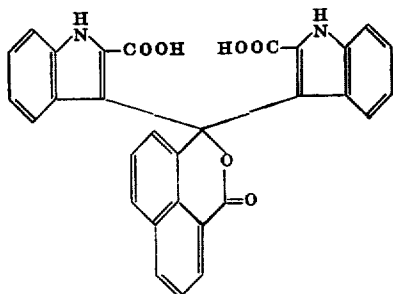
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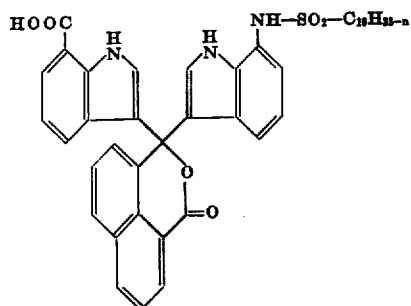
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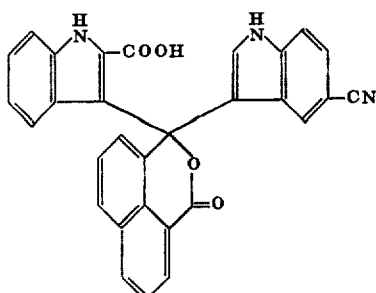
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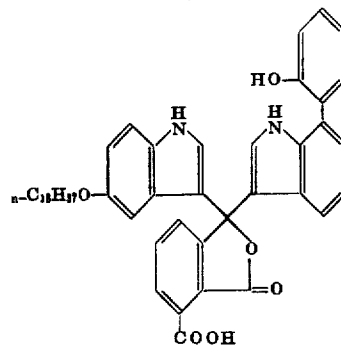
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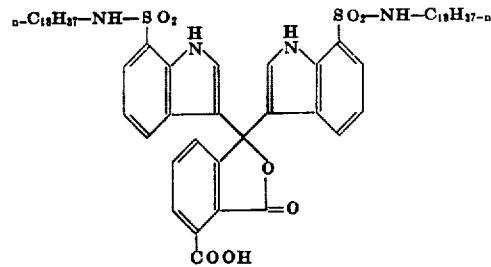
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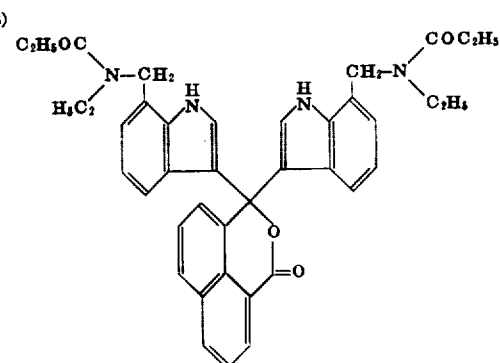
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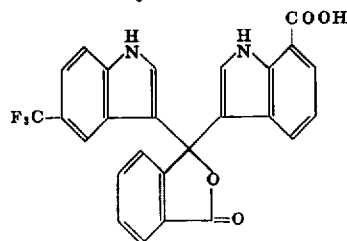
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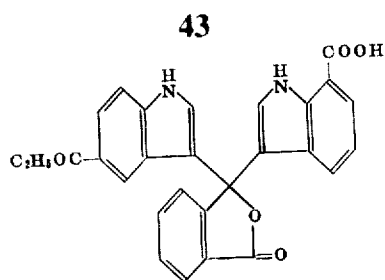
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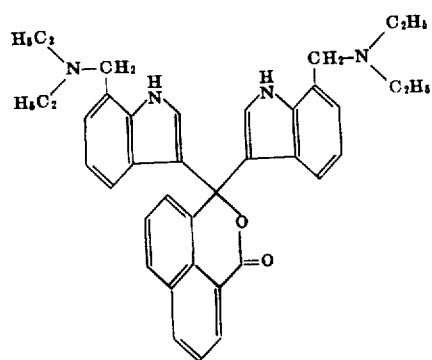
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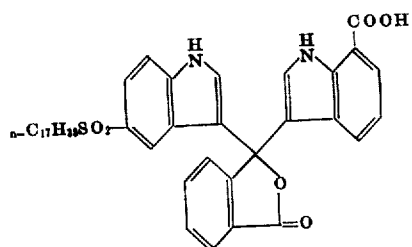
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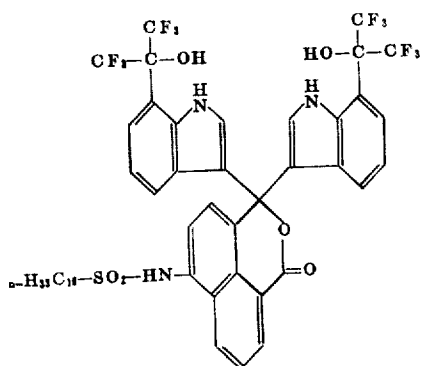
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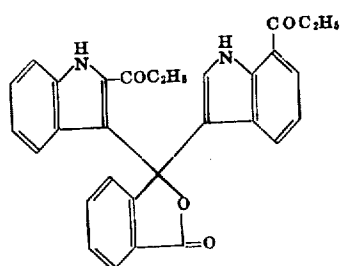
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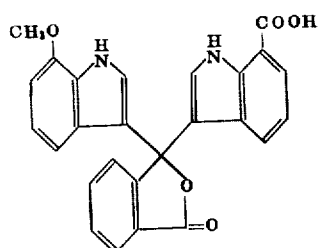
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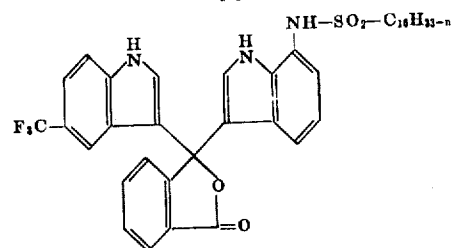
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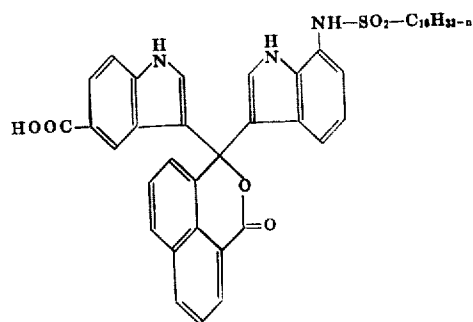


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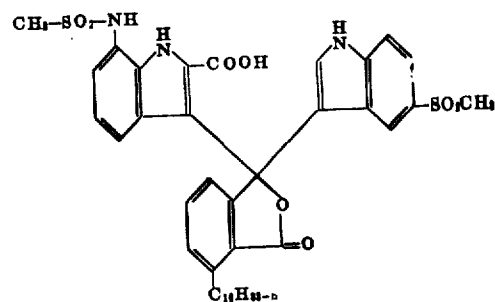
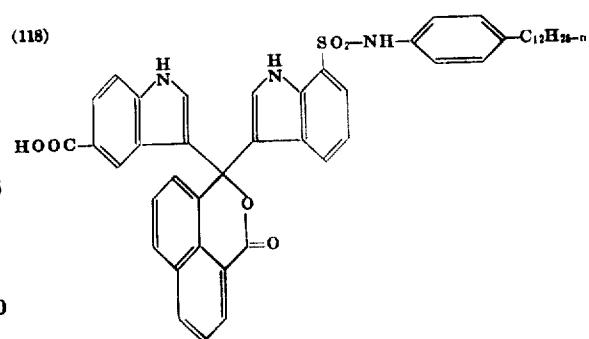
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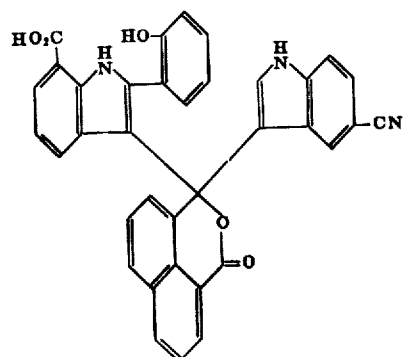
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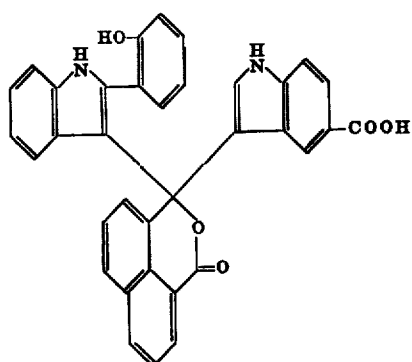


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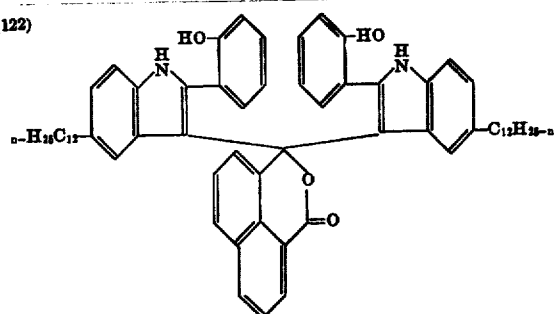


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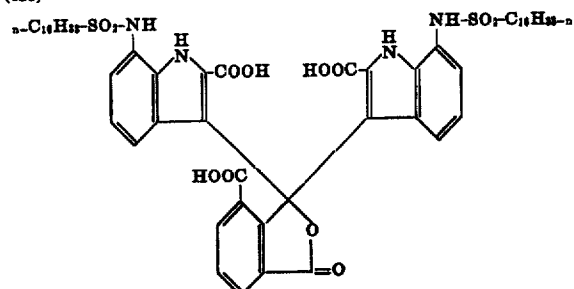
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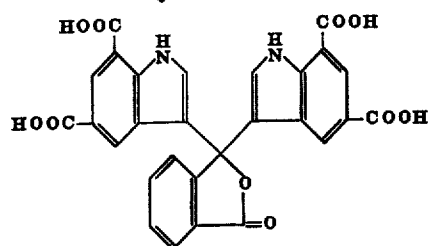
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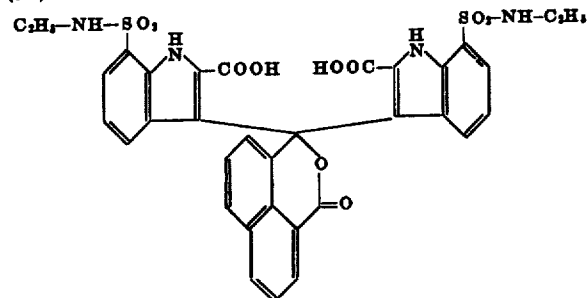
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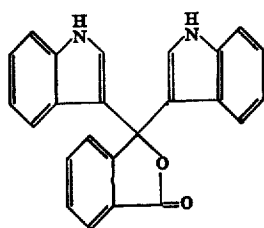
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(125)



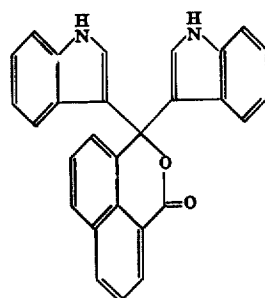
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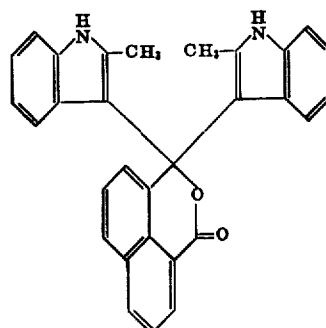
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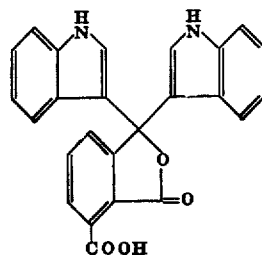
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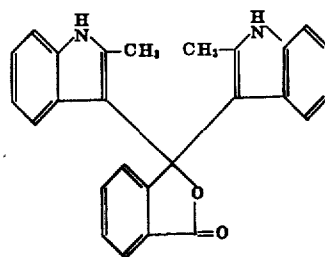


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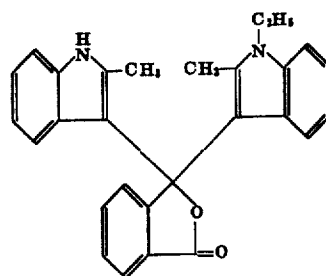
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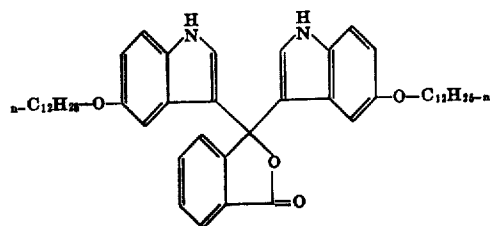


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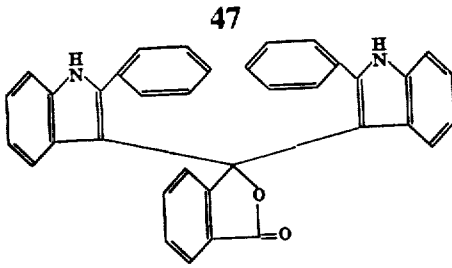
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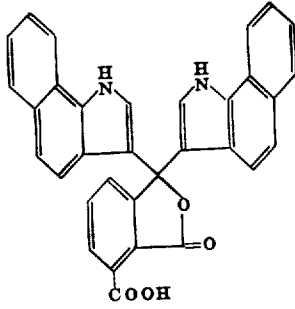


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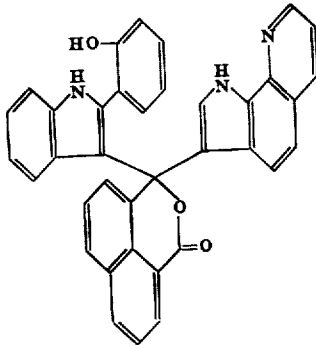
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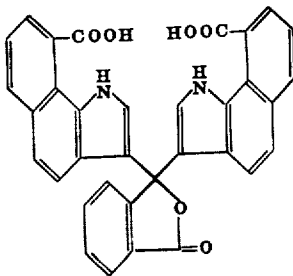
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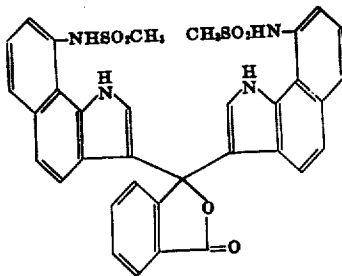
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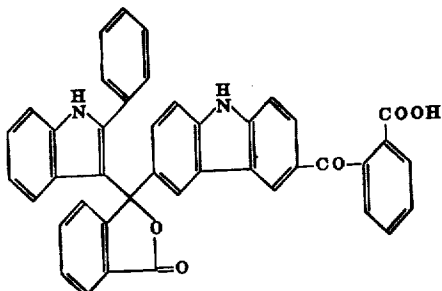
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(137)

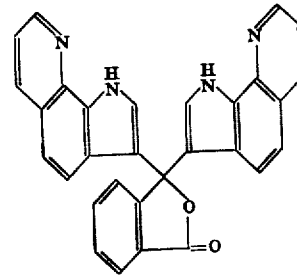


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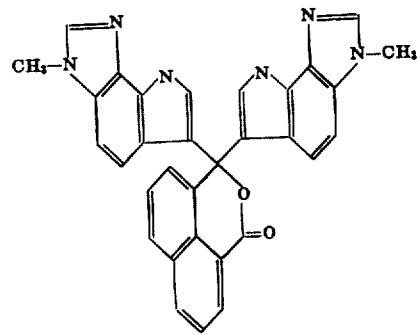
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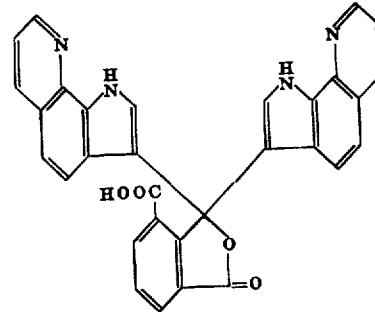
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(141)

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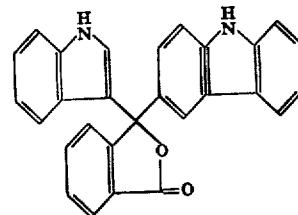
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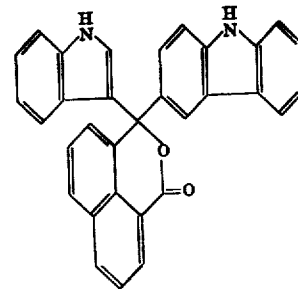
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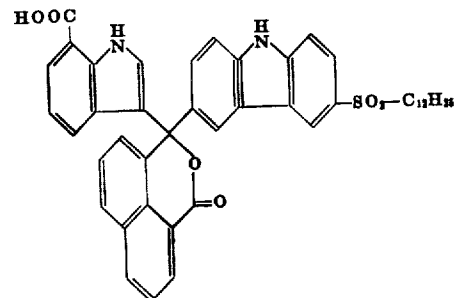
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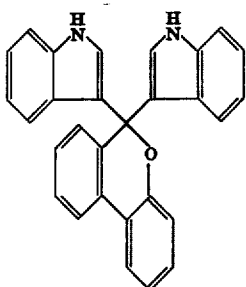


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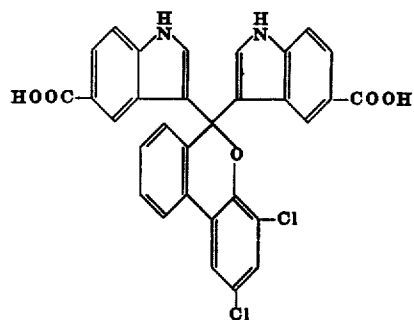
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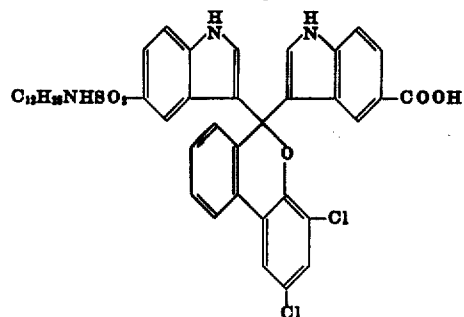
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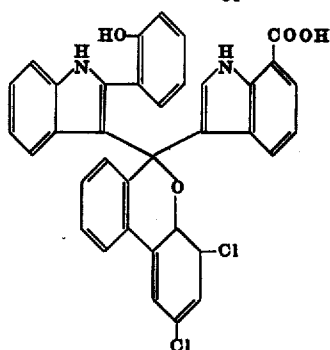
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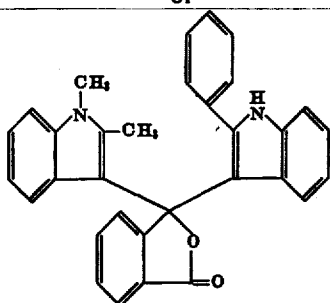
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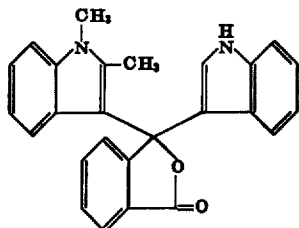
(148)



(149)

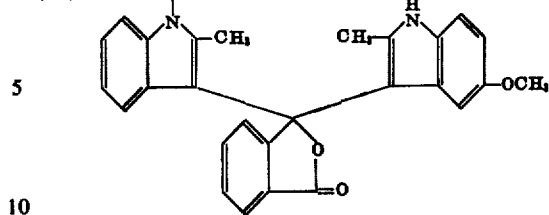


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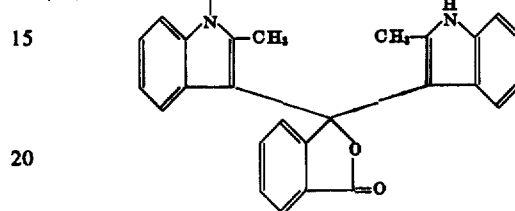


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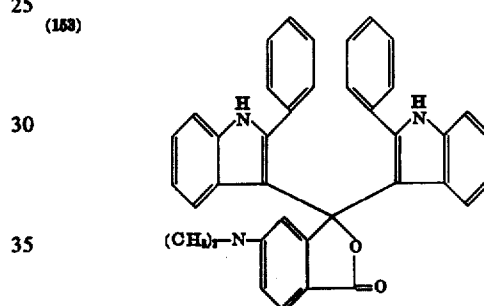
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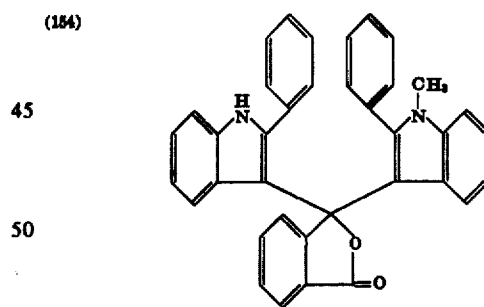
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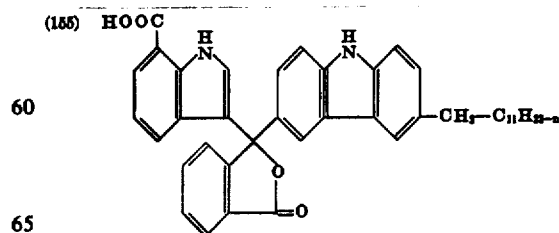
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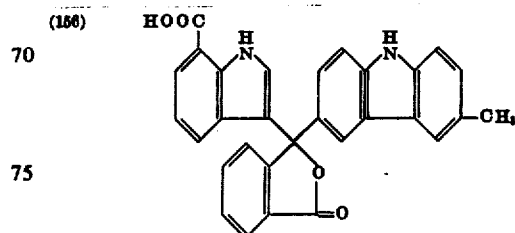
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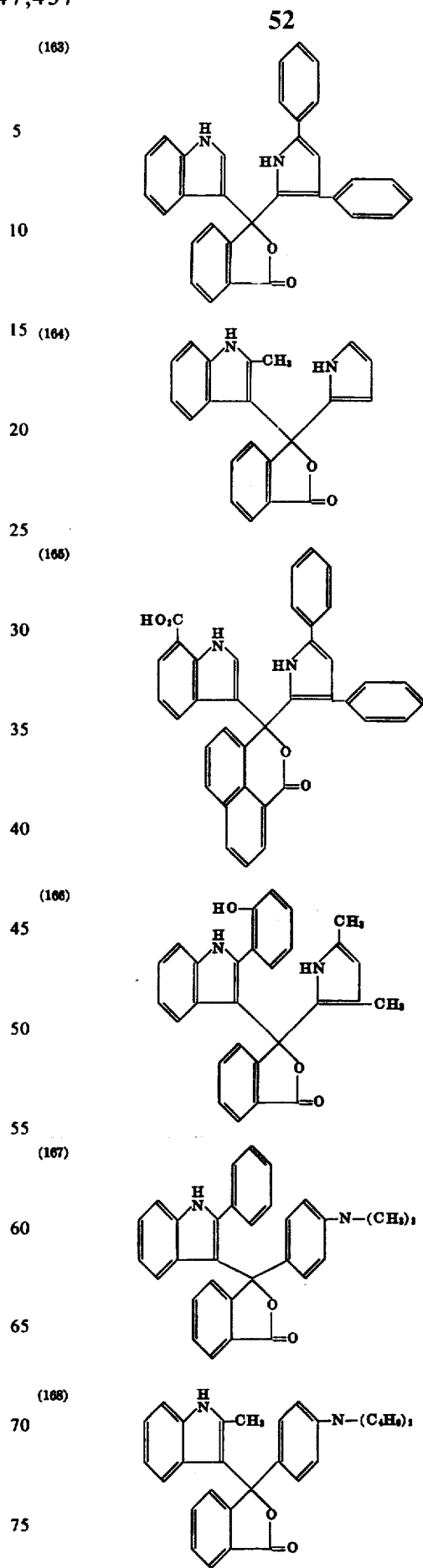
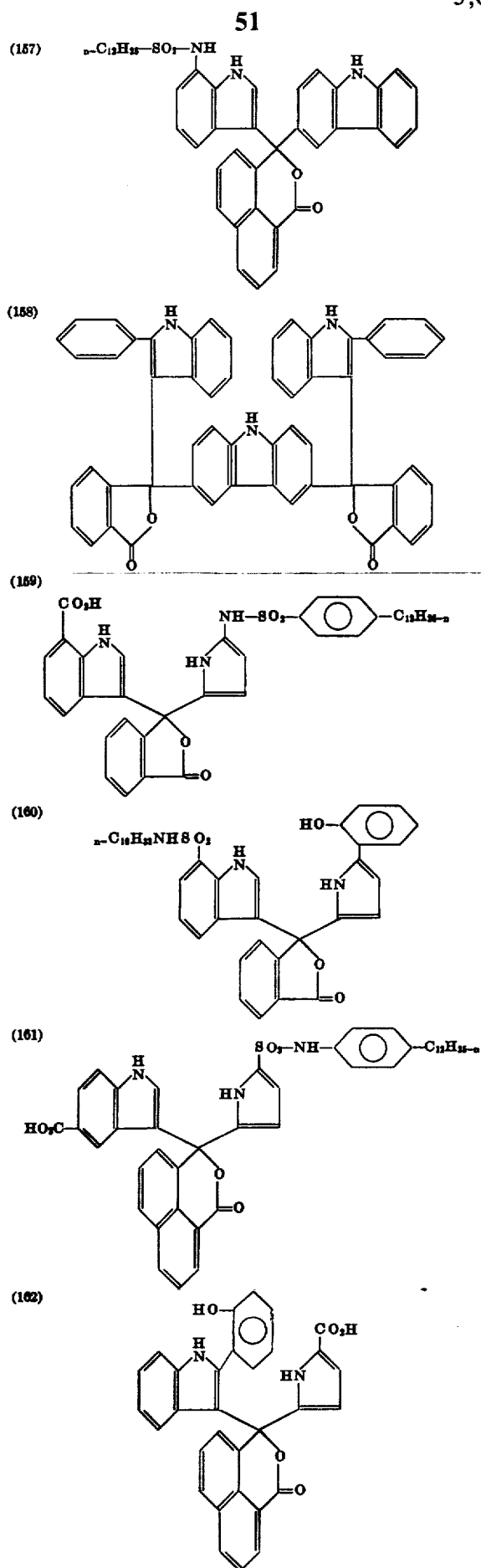


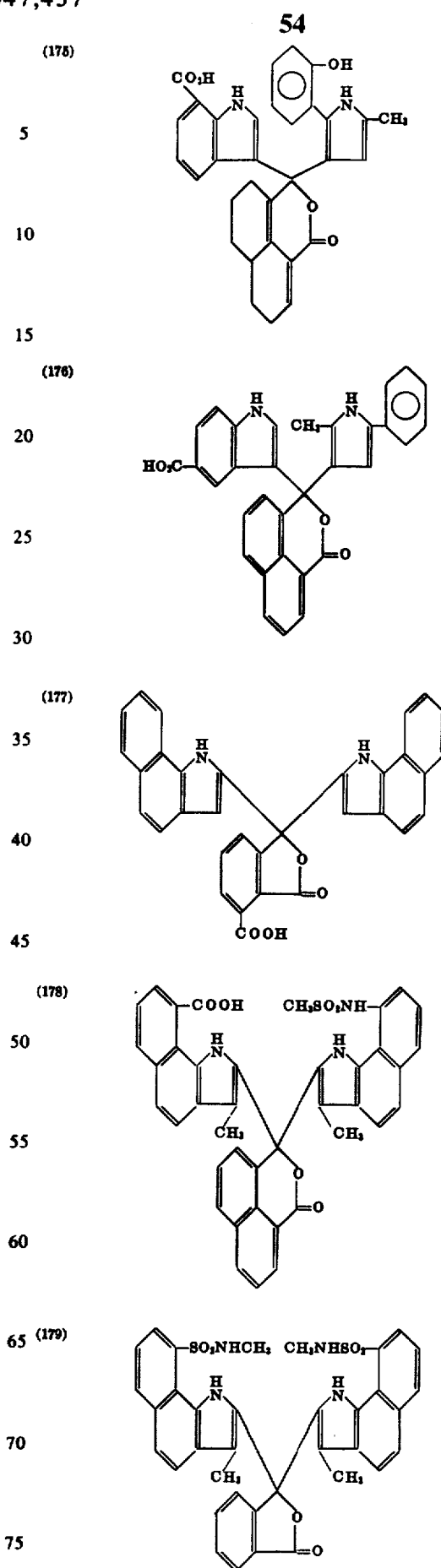
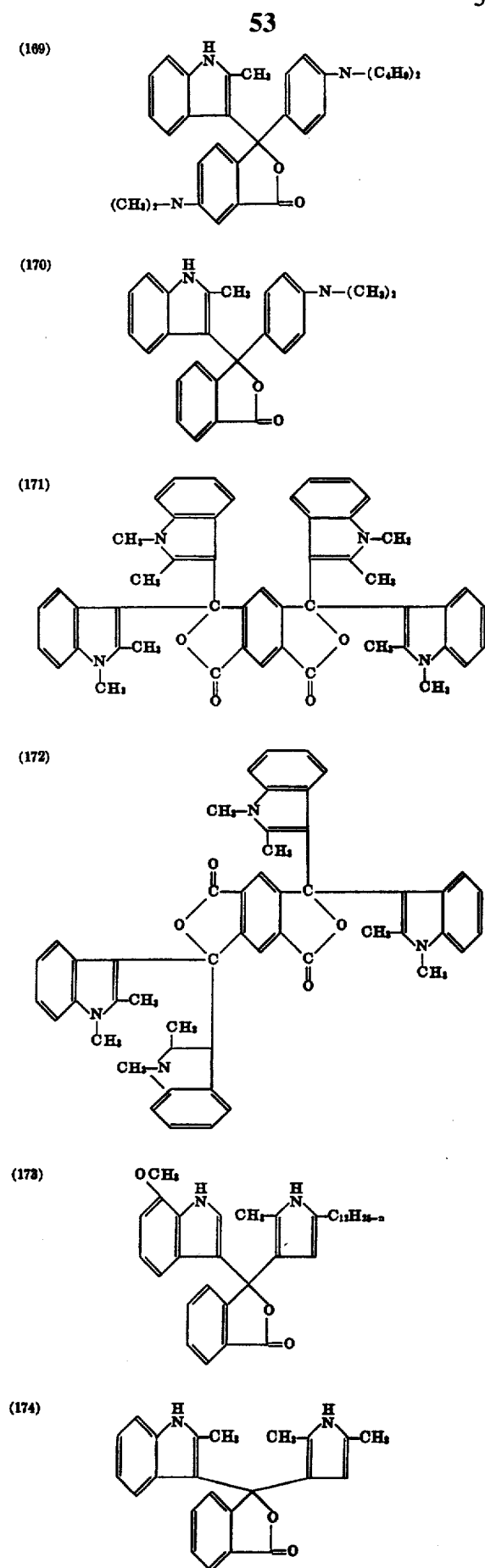
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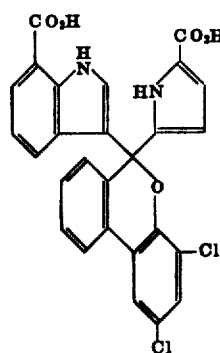
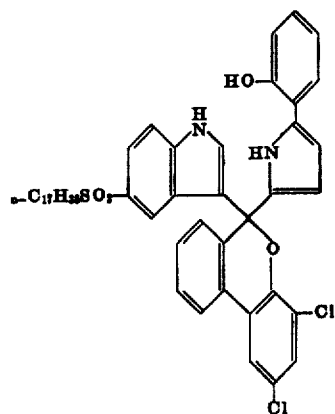
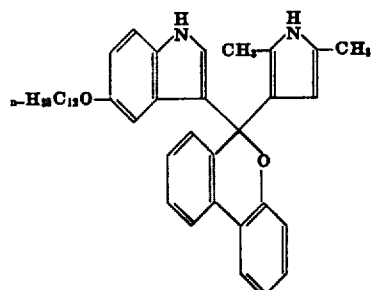
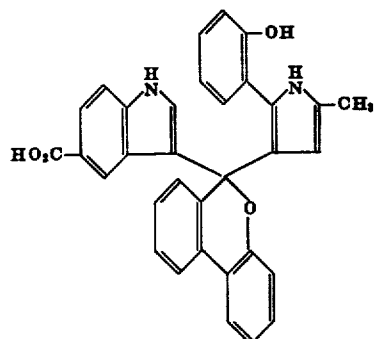
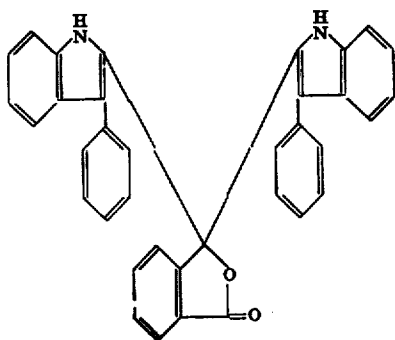
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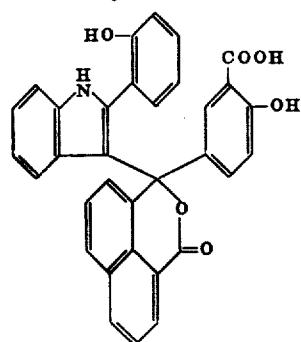
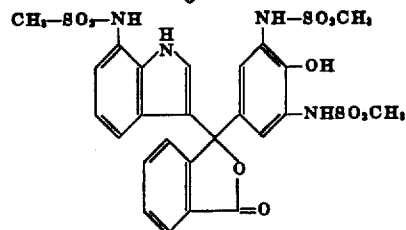
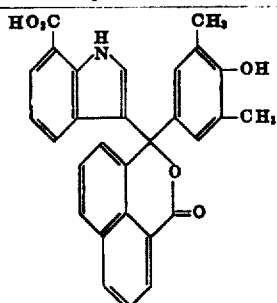
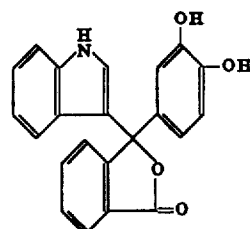
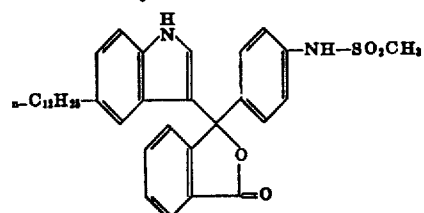
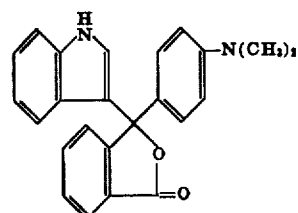
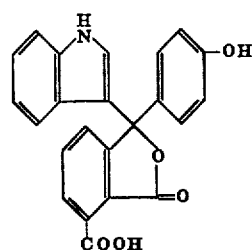


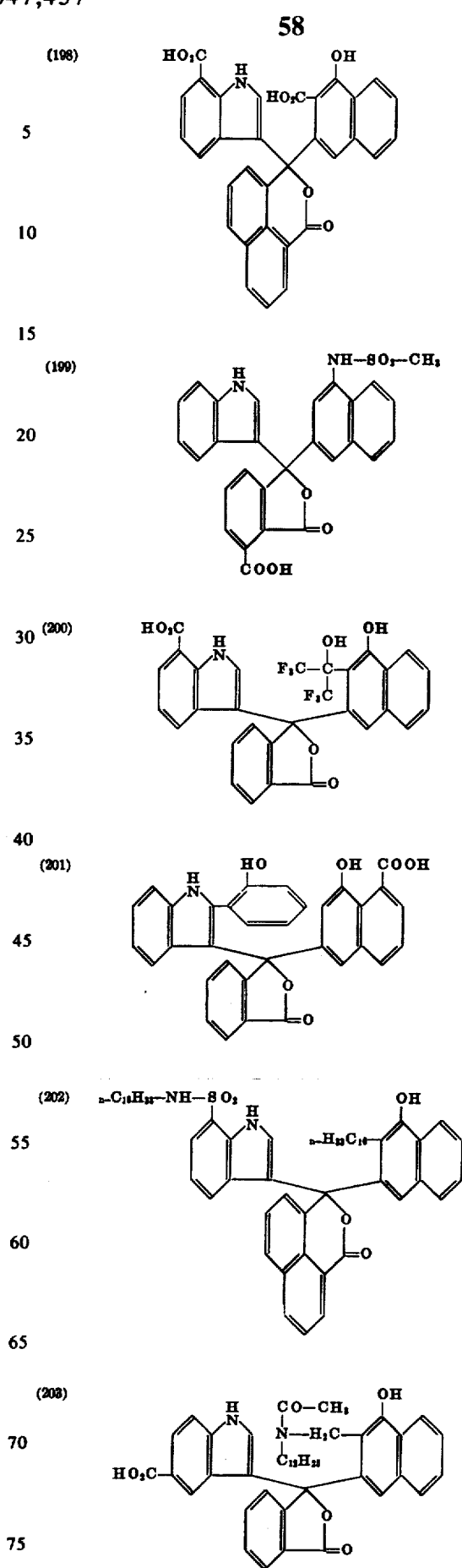
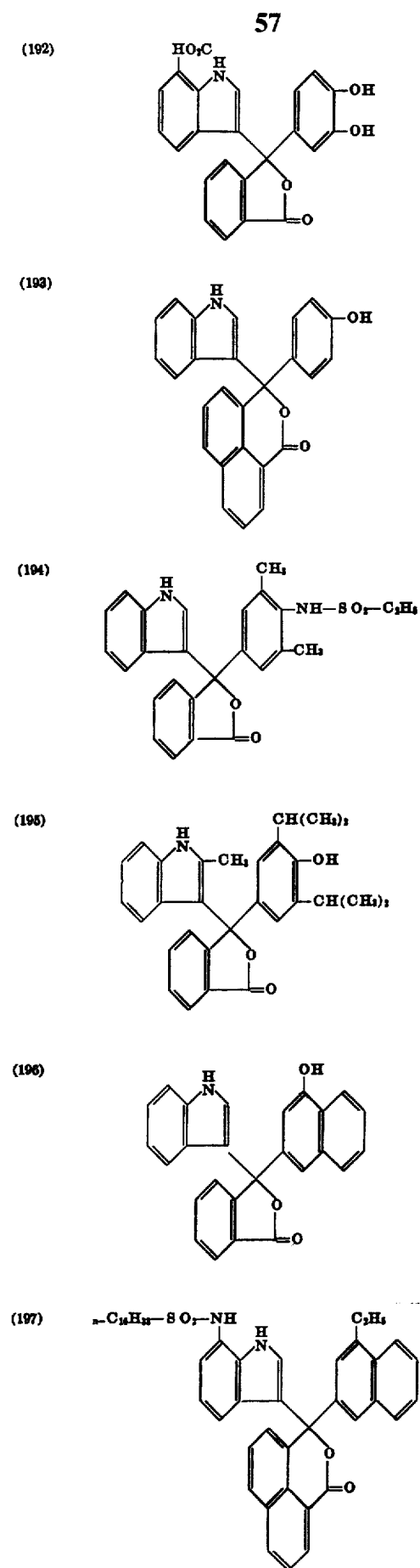


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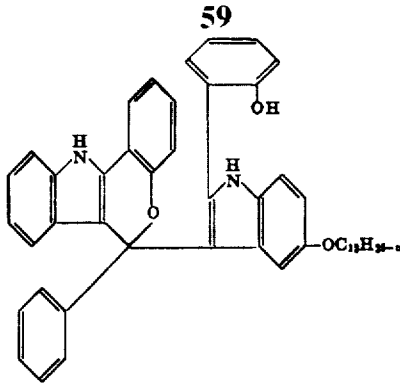


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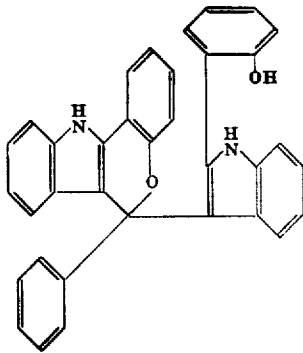




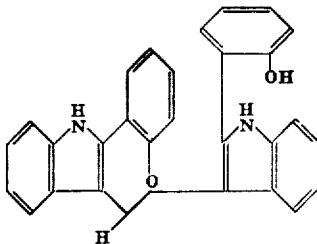
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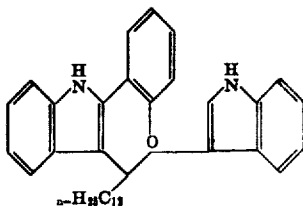
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As disclosed and claimed in my copending application, Ser. No. 43,782 filed June 5, 1970, (now abandoned and of which the present application is in part a continuation), it has been quite unexpectedly discovered that an improved film unit assemblage of the aforementioned general structural parameters and adapted to be processed, subsequent to photoexposure, in the presence of actinic radiation may be fabricated to employ, as the opacifying means interposed intermediate the reception layer and next adjacent silver halide layer subsequent to photoexposure, an inorganic light-reflecting pigment dispersion containing reflecting pigment in a concentration per se insufficient, distributed as a layer intermediate the reception layer and next adjacent silver halide layer, to effectively prevent transmission of radiation actinic to the silver halide layer therethrough and at least one optical filter agent, at a pH above the pKa of the optical filter agent, in a concentration per se also insufficient to prevent transmission of actinic radiation therethrough, which concentrations individually and additively are together insufficient to prevent transmission of incident actinic radiation but in admixture are synergistically effective to provide a barrier to such transmission. Specifically, the inorganic light-reflecting pigment dispersion containing the optical filter agent is formulated to exhibit an optical transmission density $>\sim 6.0$ density units and an optical

reflection density $<\sim 1.0$ density units at a pH above the pKa of the optical filter agents included.

In accordance with that discovery, the optical filter agent will be employed in a concentration, itself ineffective to provide the required transmission density alone or, theoretically, in combination with the inorganic light-reflecting pigment, as projected by Beer's Law, that is, $D_T = EC/l$ wherein D_T is transmission density, E is the epsilon of the optical filter agent, C is the concentration and l is the radiation path length, but empirically effective in combination with the pigment to prevent transmission of radiation actinic to the silver halide layers incident on the layer comprising the dispersion, during processing in the presence of actinic radiation, and sufficiently low to provide substantially immediate viewing of transfer image formation against the background provided by the reflecting pigment. Such effective minimal concentration of filter agent specifically facilitates the acceleration of the clearing time involved in discharging from visual observation the filter agent employed by reduction of the environmental pH as detailed above from above to below the pKa of the filter agent selected.

The film unit assemblage constructed in accordance with this discovery is specifically adapted for processing in the presence of actinic radiation by reason of the protection afforded the silver halide layer's exposure surface by the presence of the pigment dispersion protecting from exposure such surface, and for the simultaneous viewing of the transfer image carried by the reception layer by reason of the minimal optical reflection density exhibited by the light-reflecting pigment layer, subsequent to photoexposure of the silver halide layer and formation of the pigment layer. There is thus provided substantially immediate viewing of transfer image formation against a reflecting pigment layer background exhibiting minimal contamination provided by the minor concentration of substantially masked optical reflecting agent now discovered to be necessary to prevent transmission of fog-producing actinic radiation through the reflecting layer and thus protecting the silver halide layer during transfer processing. The *de minimus* concentration of optical filter agent unexpectedly discovered to be capable of effective employment to prevent light transmission when dispersed in intimate relationship with reflecting pigment optimizes discharge of the minimal reflectivity contamination as is so provided by the agent upon decrease of the environmental pH from that at which the optical filter agent absorbs radiation to that at which such agent is substantially innocuous optically.

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) reflecting layers provided by processing compositions containing titanium dioxide dispersed in water in a concentration to give about 1,500 to 4,000 mg./ft.² of titanium dioxide when solidified 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 ~ 85 percent.

In embodiments wherein the dispersion comprises a preformed layer positioned intermediate the reception layer and next adjacent silver halide 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 $<\sim 0.2$ micron in diameter and preferably $<\sim 0.2$ micron in diameter and preferably $<\sim 0.05$ micron 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 in excess of ~ 0.2 micron in diameter and will be coated at a coverage of ~ 200 to 1,000 mg./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

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with the silver halide 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 postprocessing 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 halide layers in order to provide effective protection against 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 must 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 must possess a pKa below that of the processing pH and above that of the environmental pH subsequent to transfer image formation, and will be selected for employment in the minimum concentration necessary to provide an optical transmission density $> \sim 6.0$, at wavelengths at which the silver halide layer is maximally responsive, and in no instance an optical reflection density $< \sim 1.0$ at such wavelengths.

As examples of such pH-sensitive optical filter agents adapted for employment in the practice of the preferred embodiment utilizing the above synergistic effect, mention may be made of:

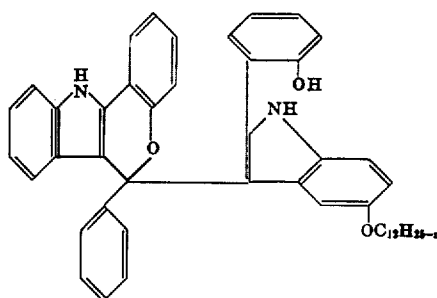
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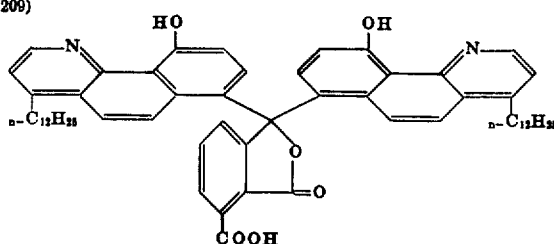


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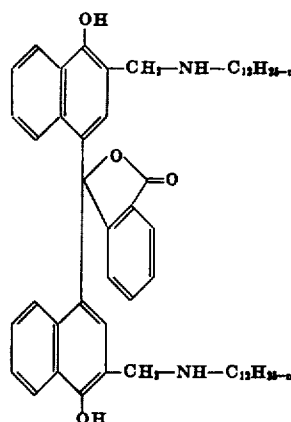
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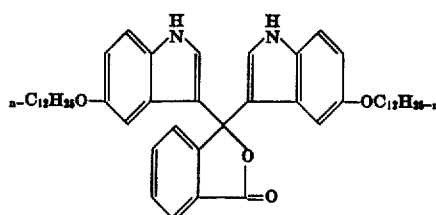
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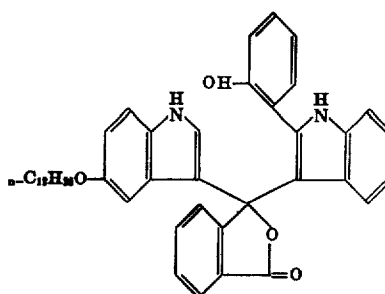
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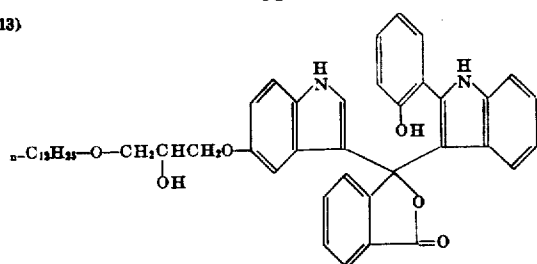


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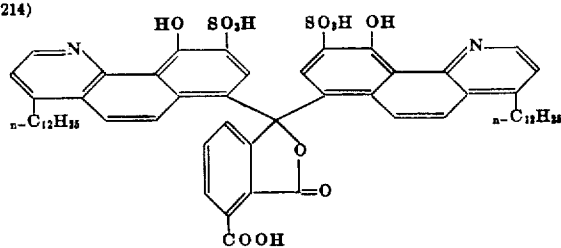


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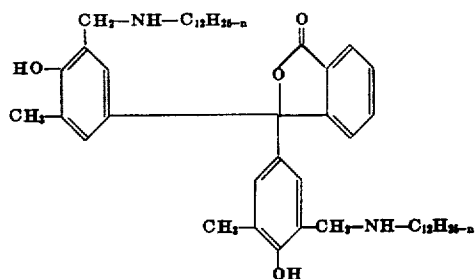
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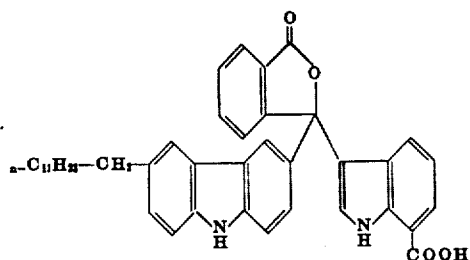


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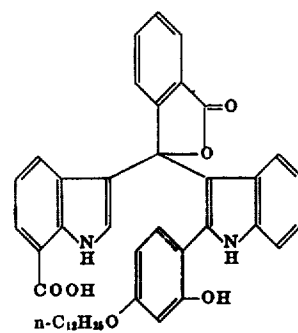
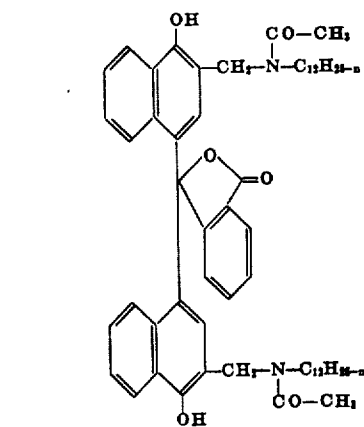
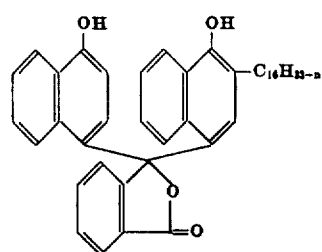
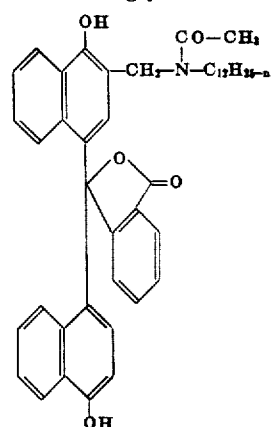
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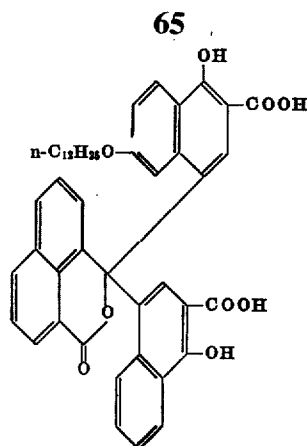
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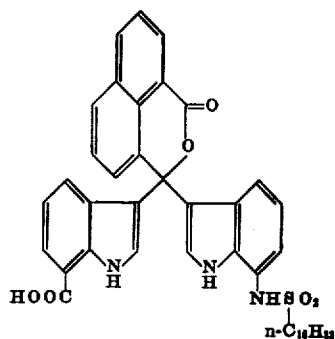
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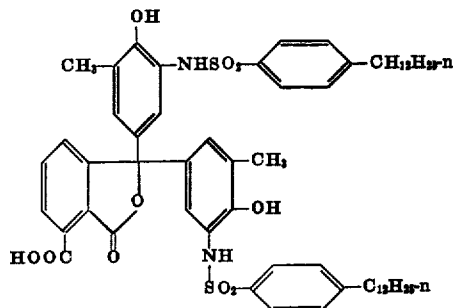
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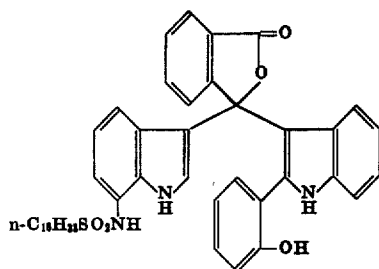
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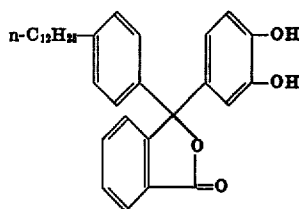
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In general, preferred agents, both opacifying and filter, are those which remain immobile within their respective compositions during and subsequent to photographic processing and particularly those which comprise insoluble and nondiffusible materials.

A multicolor embodiment of this invention may be practiced by use of a film unit like that shown in FIGS. 3 and 4 and prepared by coating, in succession on a gelatin-subbed, 4-mil. opaque polyethylene terephthalate film base, the following layers:

1. a layer of the cyan dye developer 1,4-bis-(β -[hydroquinonyl- α -methyl]-ethylamino)-5,8-dihydroxy-anthraquinone dispersed in gelatin and coated at a coverage of about 80 mg./ft.² of dye and about 100 mg./ft.² of gelatin;
2. a red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 225 mg./ft.² of silver and about 50 mg./ft.² of gelatin;
3. a layer of the acrylic latex sold by Rohm and Haas Co., Philadelphia, Pennsylvania, U.S.A., under the trade designation AC-61 and polyacrylamide coated at a coverage of about 150 mg./ft.² of AC-61 and about 5 mg./ft.² of polyacrylamide;
4. a layer of the magenta dye developer 2-(p-[β -hydroquinonyl-ethyl]-phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of 70 mg./ft.² of dye and about 120 mg./ft.² of gelatin;
5. a green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 120 mg./ft.² of silver and 60 mg./ft.² of gelatin;
6. a layer comprising the acrylic latex sold by Rohm and Haas Co. under the trade designation B-15 and polyacrylamide coated at a coverage of about 100 mg./ft.² of B-15 and about 10 mg./ft.² of polyacrylamide;
7. a layer of the yellow dye developer 4-(p-[β -hydroquinonyl-ethyl]-phenylazo)-3-(N-n-hexyl-carboxamido)-1-phenyl-5-pyrazolone and the auxiliary developer 4'-methylphenyl hydroquinone dispersed in gelatin and coated at a coverage of about 50 mg./ft.² of dye, about 15 mg./ft.² of auxiliary developer and 50 mg./ft.² of gelatin;
8. a blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 75 mg./ft.² of silver and about 75 mg./ft.² of gelatin; and
9. a layer of gelatin coated at a coverage of about 50 mg./ft.² of gelatin.

Then a transparent 4-mil. polyethylene terephthalate film base may be coated, in succession, with the following illustrative layers:

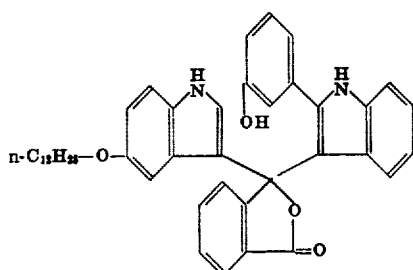
1. a 7:3 mixture, by weight, of polyethylene/maleic acid copolymer and polyvinyl alcohol at a coverage of about 1,400 mg./ft.², to provide a polymeric acid layer;
2. a graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mg./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 900 mg./ft.² and including about 20 mg./ft.² phenyl mercapto tetrazole, 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.

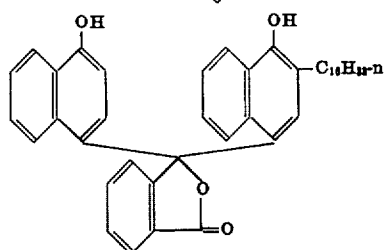
A rupturable container comprising an outer layer of lead foil and an inner liner or layer of polyvinyl chloride retaining an aqueous alkaline processing solution comprising:

Water	100	cc.
Potassium hydroxide	11.2	g.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4	g.
N-phenethyl- α -picolinium bromide	2.7	g.
Benzotriazole	1.15	g.
Titanium dioxide	50.0	g.
	2.08	g.

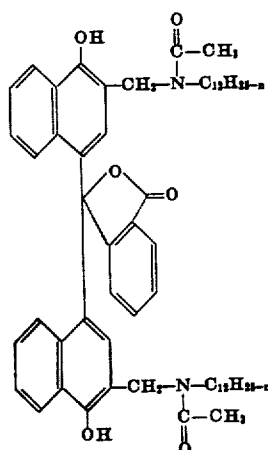
(A)



(B)



(C)



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 gelatin layer.

The photosensitive composite film units may be exposed through step wedges to selectively filter radiation incident on the transparent polyethylene terephthalate layer 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. During processing, the multicolor dye transfer image formation may be viewed through the transparent polyethylene terephthalate layer against the titanium dioxide background provided by distribution of the pigment-containing processing composition between layer 53 and the polymeric image-receiving layer. Multicolor dye transfer image formation will be found to be substantially completed and exhibiting the required color brilliance, hues, saturation and isolation, within a period of approximately 90 seconds. The image formation may be immediately viewed upon distribution of the processing composition by reason of the protection against incident radiation afforded the photosensitive silver halide emulsion layers by the composition's optical transmission density of $> \sim 6.0$ density units and against the titanium dioxide's effective reflective background afforded by reason of the composition possessing an optical reflection density $< \sim 1.0$ density units.

Reference may be made to FIGS. 14 through 17, inclusive, which specifically denote graphically decrease in optical reflection density per unit processing time effected by reason of in situ reduction of such a film unit's pH from an initial pH above the pKa of the respective optical filter agents described above to a pH substantially below the pKa of the respective agents.

Specifically, FIG. 14 and Curve A of FIG. 17 denote the clearing time (decrease in optical reflection density) of above-identified optical filter agent A above wherein FIG. 14 denotes the clearing time throughout the spectral absorption range of the agent and FIG. 17 denotes clearing time as a function of optical density at the λ_{max} of the respective compound. FIG. 15 and Curve B of FIG. 17 and FIG. 16 and Curve C of FIG. 17 provide analogous graphic illustrations of optical density per unit processing time of above-identified optical filter agents B and C during the described performance of a photographic diffusion transfer process comprising the present invention.

The initial optical transmission density provided by a processing composition substantially as above at the respective λ_{max} of the last-identified optical filter agents measure in situ as a composite formulation comprises ~ 6.2 , 6.2 and 6.1 , respectively, of which ~ 1.25 , 1.15 and 1.10 , respectively, is contributed by the titanium dioxide content of the processing composition, the remainder contributed by the optical filter agents at a pH above their respective pKa.

In the absence of the titanium dioxide, the measured optical density provided by the optical filter agents in combination at their respective λ_{max} comprises ~ 2.4 , 2.05 and 2.3 . It will be apparent that the optical densities of the optical filter agent individually added to the optical density of the titanium dioxide is insufficient theoretically to provide the required minimum optical transmission density of $> \sim 6.0$ density units, but has been found, by means of the present invention, to unexpectedly provide in combination an optical density in accordance with the mathematical expression $D_T = EC(1 + \Delta I)$, wherein D_T , E , C , I are as defined above; thus directly providing the unexpected advantageous end results discussed in detail above.

The pH and solvent concentration of the alkaline processing solution initially employed must possess a pH above the pKa of the optical filter agents, 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 $> \sim 11$ and most preferably $> \sim 12$ 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 about 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 will 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 disposed within the film unit or a polymeric acid layer, for example, a polymeric acid layer approximating 0.3 to 1.5 mil. in thickness, positioned inter-

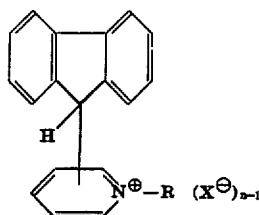
mediate the transparent support and image-receiving layer, and/or the opaque support and next adjacent emulsion/dye unit layer, and the film unit may also contain a polymeric spacer or barrier layer, for example, approximating 0.1 to 0.7 mil. in thickness, next adjacent the polymeric acid layer, opposite the respective support layer, as previously described.

It will be understood that in the performance of the present invention that the silver halide layers should be protected in all visible and nonvisible regions of the spectrum to which they are sensitive. Depending upon the sensitivity of the silver halide or other photosensitive material employed, it may be desirable to use ultraviolet and/or infrared absorbers in conjunction with the dye or dyes selected as optical filter agents to provide additional protection in the the nonvisible regions. Ultraviolet and infrared absorbers are well known in the photographic art and any of the compounds conventionally used for this purpose may be employed in the present invention. Like the optical filter agents, the absorbers should provide the desired protection against postexposure fogging during at least the initial stages of development but should not absorb radiation intended to selectively expose the photosensitive material or detract from the brilliance, hues and other properties of the final image. Thus, the absorber or absorbers, as will be appropriate for the particular compounds selected, may be initially disposed in a layer of the film unit and/or the processing solution and subsequent to processing may be retained in or separated from the final product.

The image-forming materials transferred to provide the desired transfer image may themselves assist in providing the desired postexposure light protection. For example, where the image is formed from transferred dye developers, the visible absorption of the transferred dye developers is effective to assist in absorbing incident radiation and thus help to prevent post exposure fog. It is particularly significant, e.g., where the photosensitive material is the usual developing out silver halide emulsion, that the transferred dye developers transfer from unexposed areas and are deposited in a position effective to absorb light which otherwise might expose said unexposed areas. Because of this optical relationship, the density provided by transferred image-forming material may be taken advantage of to discharge the color of the optical filter agent earlier than it otherwise might be desirable to do.

An additional group of optical filter agents which may be used in accordance with this invention include a 9-pyridyl fluorene optical filter agent and preferably a 9-(N-alkyl-pyridyl)-fluorene agent of the formula:

(A)



wherein R is an alkyl group; X is an anion; and n is the integer 1 when R is negatively charged and the integer 2 when R is electrically neutral; these optical filter agents are the subject of the copending application of Alan L. Borrer, Ser. No. 49,627, filed June 25, 1970.

In particularly useful embodiments of this invention, the transparent support contains a small quantity of a pigment, e.g., carbon black, to prevent fog formation by light piping of actinic light incident upon an edge thereof; such elements are described and claimed in the copending application of Edwin H. Land, Ser. No. 101,842 filed Dec. 28, 1970. Similarly, fog from light piping may be avoided by incorporating an alkali-dischargeable dye in a suitable layer, e.g., the image-receiving layer, in accordance with the disclosure of the copending application of Howard G. Rogers, Ser. No. 101,842 filed Dec. 28, 1970.

It is advantageous in the performance of diffusion transfer processes to chemically prevent (i.e., restrain or arrest)

development of both unexposed silver halide and exposed but not yet developed silver halide after sufficient development has been achieved to properly modulate the formation of the desired imagewise distribution of the image-forming color-providing material. One method of achieving this result is to place a suitable development restrainer in a layer of the film unit such that it is made available to react with the undeveloped silver halide and render it substantially undevelopable after a predetermined period, in accordance with the disclosure of U.S. Pat. No. 3,265,498 issued Aug. 9, 1966 to Howard G. Rogers and Harriet W. Lutes. A particularly useful development "stopper" is 1-phenyl-5-mercaptotetrazole initially positioned in the image-receiving layer. Use of such delayed-availability development stopping techniques makes it possible to discharge the color of the optical filter agent(s) earlier, since the silver halide is thereby rendered essentially inert to light that otherwise would fog it.

It will be recognized that the embodiment shown in FIG. 18 may be modified by omitting the colorless alkali-activated optical filter agent layer 60 and including the appropriate optical filter agent(s) in the processing composition 17. In yet another modification, said layer 60 may be placed between the dye developer layer 12 and the layer 62 containing titanium dioxide, the cover sheet 64 being opaque.

It is also contemplated to provide to utilize a silver receptive layer positioned on the opposite side of the light-reflecting layer from the image carrying layer to provide a "sink" for silver halide not used in the formation of the desired image. Thus, for example, in a silver dye bleach process, the developed silver is used to bleach the image dye giving a positive dye image, and the unexposed silver halide is removed by diffusion to such a silver receptive layer where it is precipitated and effectively masked by the light-reflecting layer. Alternatively, the developed silver halide may provide a negative silver image per se. Similarly, the use of a dye image-receiving layer positioned on said opposite side of the light-reflecting layer may provide a sink for dye released by development of the exposed silver halide, thus providing a positive dye image in initially nondiffusible dye. In such systems, the optical filter agent may be in the processing composition and/or in appropriate layers of the film unit depending upon the particular arrangement of the layers of the film unit.

In certain instances, the color of the optical filter agent may be discharged by a diffusible acidic reagent initially positioned, e.g., the image-receiving layer, prior to reduction of the pH to a level substantially precluding further transfer of image-forming materials, in accordance with the disclosure of the copending application of Terry W. Milligan, Ser. No. 83,480, filed Oct. 23, 1970. It is also within the scope of this invention to utilize a buffer in the processing composition, in accordance with the disclosure of the copending application of Terry W. Milligan, Ser. No. 83,479 filed Oct. 23, 1970.

Discharge of an optical filter agent(s) color may be effected by use of a polymeric acid to reduce the pH as described above, by the use of a particulate acid as disclosed in the copending application of Edwin H. Land, Ser. No. 846,442 filed July 31, 1969 (now U.S. Pat. No. 3,576,625 issued Apr. 27, 1971), or by the release of an acidic reagent from a second rupturable container after a predetermined period; the use of a plurality of rupturable containers ruptured in a manner to release their contents for sequential utilization in a photographic process is well known in the diffusion transfer art, as, for example, in U.S. Pat. No. 2,607,685 issued Aug. 19, 1952 to Edwin H. Land.

The processing composition may be initially absorbed into a processing sheet or web, which sheet may also include the image-receiving layer, as described, for example, in U.S. Pat. No. 3,345,165 issued Oct. 3, 1967 to Edwin H. Land. Other techniques for providing processing compositions by use of liquid-impregnated sheets are well known in the art.

In the film units of this invention, the support layers are preferably dimensionally stable, liquid-impermeable layers which taken together possess a processing composition sol-

vent vapor permeability sufficient to effect, subsequent to substantial transfer image formation and prior to any substantial environmental image degradation to which the resulting image may be prone, osmotic transpiration of processing composition solvent in a quantity effective to decrease the solvent from a first concentration at which the color-providing material is diffusible to a second concentration at which it is not. Although these layers may possess a vapor transmission rate of 1 or less gm./24 hrs./100 in.²/mil., they preferably possess a vapor transmission rate for the processing composition solvent averaging not less than about 100 gm./24 hrs./100 in.²/mil., most preferably in terms of the preferred solvent, water, a vapor transmission rate averaging in excess of about 300 gm. of water/24 hrs./100 in.²/mil., and may advantageously comprise a microporous polymeric film possessing a pore distribution which does not unduly interfere with the dimensional stability of the layers or, where required, the optical characteristics of such layers. Such pore distribution may comprise, for example, an average pore diameter of from less than about 20 microns to greater than about 100 microns and a pore volume of less than about 3 percent to greater than 7 percent. The preferred dimensionally stable layers are designed so that there is no liquid flow through the layers while allowing the vapor of the processing composition solvent to pass by diffusion from the evaporating liquid body. As examples of useful materials of this nature, mention may be made of those rigid or flexible materials possessing the aforementioned liquid impermeability and vapor transmissivity 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; cross-linked polyvinyl alcohol; regenerated cellulose; and the like. These layers may, for example, be on the order of from about 2 to 6 mil. in thickness. Opaque support layers should have sufficient opacity to prevent fogging from occurring by light passing therethrough.

It will be noted that the liquid processing composition employed with dye developer processes may contain an auxiliary or accelerating developing agent, such as p-methylaminophenol, 2,4-diamino-phenol, p-benzylaminophenyl, hydroquinone, toluhydroquinone, phenylhydroquinone, 4'-methylphenylhydroquinone, etc. It is also contemplated to employ a plurality of auxiliary or accelerating developing agents, such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed in U.S. Pat. No. 3,039,869, issued June 19, 1962. As examples of suitable combinations of auxiliary developing agents, mention may be made of 1-phenyl-3-pyrazolidone in combination with p-benzylaminophenol and 1-phenyl-3-pyrazolidone in combination with 2,5-bis-ethylenimino-hydroquinone. Such auxiliary developing agents may be employed in the liquid processing composition or they may be initially incorporated, at least in part, in any one or more of the silver halide emulsion strata, the strata containing the dye developers, the interlayers, the overcoat layer, the image-receiving layer, or in any other auxiliary layer, or layers, of the film unit. It may be noted that at least a portion of the dye developer oxidized during development may be oxidized and immobilized as a result of a reaction, e.g., an energy transfer reaction, with the oxidation product of an oxidized auxiliary developing agent, the latter developing agent being oxidized by the development of exposure silver halide. Such a reaction of oxidized developing agent with unoxidized dye developer would regenerate the auxiliary developing agent for further reaction with the exposed silver halide.

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 photosensitive 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 photographic 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. Pat. Nos. 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.

The inventive concepts herein disclosed may also be used in combination with desensitizing agents i.e., reagents which render residual unexposed silver halide substantially unexposable within the parameter of the process conditions, the use of which is disclosed and claimed in the copending application of Edwin H. Land, Howard G. Rogers and Richard W. Young, Ser. No. 745,749 filed July 18, 1968 (now U.S. Pat. No. 3,579,333 issued May 18, 1971).

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, possess 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 had 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; issued July 28, 1953; 2,661,293, issued Dec. 1, 1953; 2,698,244, issued Dec. 28, 1954; 2,698,798 issued Jan. 4, 1955; and 2,802,735, issued Aug. 13, 1957, wherein color diffusion transfer processes are described which employ color-coupling techniques comprising, at least in part, reacting one or more color-developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Pat. No. 2,774,668, issued Dec. 18, 1956, wherein color diffu-

sion 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 continuous image-receiving layer, and including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse or provide diffusible image-providing materials during processing as a function of development.

For the production of the photosensitive gelatino silver halide emulsions employed to provide the film unit, the silver halide crystals 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 bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant water-soluble salts 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 after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin 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 halide 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.

The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of silver, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver chloriodobromide or silver iodobromide, of varying halide ratios and varying silver concentrations.

As the binder for the respective emulsion strata, the aforementioned gelatin may be, in whole or in part, replaced with some other colloidal material such as albumin; casein; or zein; or resins such as a cellulose derivatives, as described in U.S. Pat. Nos. 2,322,085 and 2,327,808; polyacrylamides, as described in U.S. Pat. No. 2,541,474; vinyl polymers such as described in an extensive multiplicity of readily available U.S. and foreign patents, etc.

In preferred embodiments of the present invention, the photosensitive silver halide emulsions employed will be emulsions adapted to provide a Diffusion Transfer Process Exposure Index $> \sim 50$, which index indicates the correct exposure rating of a diffusion transfer color process at which an exposure meter, calibrated to the ASA Exposure Index, must be set in order that it give correct exposure data for producing color transfer prints of satisfactorily high quality. The Diffusion Transfer Process Exposure Index is based on a characteristic H&D curve relating original exposure of the photosensitive silver halide emulsions to the respective curve densities forming the resultant transfer image. Thus, the Diffusion Transfer Exposure Index is based on the exposure to which the photosensitive silver halide emulsions for use in color diffusion transfer processes, must be subjected in order to obtain

an acceptable color transfer image by that process and is a direct guide to the exposure setting to be entered in a camera in order to obtain proper exposure of the film unit.

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 or dye developer and the use of a mixture of dyes or 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 transparency. In this case, the latent image in the photosensitive emulsion layers will be a positive and the dye image produced on the image-carrying layer will be a negative. The expression "positive image" is intended to cover such an image produced on the image-carrying layer.

It will be recognized that, by reason of preferred film unit's structural parameters, the transfer image formed following exposure of the film unit to a selected subject and processing, will be a geometrically reversed image of the subject. Accordingly, to provide geometrically nonreversed transfer images, exposure of such film unit should be accomplished through an image-reversing optical system, such as in 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 its support.

In the embodiments described above, the processing composition included a film-forming polymer which imparted viscosity and when solidified provide a polymeric bonding capacity holding together the opposing surfaces of the elements forming the ultimate laminate. It will be understood that one may also use a nonviscous processing composition and obtain a similar laminate, particularly if the surface of one of the superposed elements contacted by the processing composition has a coating thereon of a polymer, e.g., sodium carboxymethyl cellulose, soluble in said processing composition.

Such nonviscous processing compositions also may be provided by use of so-called processing webs containing the processing composition absorbed therein or by use of rupturable microcapsules.

Although in the preferred embodiments of this invention the processing composition containing the optical filter agent is distributed between two layers of the film unit being processed, it is also contemplated that one may apply a layer of a viscous processing composition to the surface of a suitable photosensitive element, e.g., one containing a preformed reflecting layer and a polymeric acid layer, the polymeric layer resulting from solidification of the viscous processing composition adhering to the surface of the photosensitive element and the color of the optical filter agent being discharged by alkali neutralization to permit viewing the final image through said polymeric layer.

An opaque layer may be provided as the support for a photosensitive element so processed to prevent exposure from the back; such an opaque layer may be permanent or temporary, e.g., a peelable black back.

Most commercial useful photographic processes are performed at an alkaline pH and the above description of the invention has been so oriented in referring to optical filter agents whose color is discharged by a reduction in pH. It will be understood, however, that the principles of this invention are also applicable to photographic processes performed at a neutral or acidic pH; in such instances, the optical filter agent is selected on the basis of it absorbing appropriate light at said process pH and becoming colorless at a more alkaline pH. The requisite increase in pH in such situations may be obtained by a delayed release of an appropriate alkaline reagent within the film unit, e.g., by extraction of an alkaline reagent encapsulated in a layer of the film unit, or by application from a second pod of a more alkaline composition distributed between appropriate layers and also retained within the laminate.

The spend pod 16 may remain attached to the final laminate or it may be severed therefrom.

It will be expressly understood that the monochrome embodiments shown, e.g., in FIGS. 1, 5, 6, 7, 8, 9 and 10, depict monochrome photosensitive elements for ease of understanding, and that multicolor photosensitive elements such as shown in FIG. 4 may be readily substituted therein by one skilled in the art.

The herein claimed subject matter may be readily distinguished from previously proposed techniques for protecting photosensitive materials from radiation actinic thereto during processing. In darkroom processing, for example, it is common practice to control the incident or environmental light by use of filters positioned over the light source, i.e., safelights, to filter out and thus exclude wavelengths actinic to the particular photosensitive material. In lieu of such safelights, it has been proposed (U.S. Pat. No. 409,618 issued Aug. 20, 1889) to add dyes to the processing solutions to similarly selectively absorb radiation actinic to the photosensitive material, transfer of the exposed photosensitive material to the processing solution being effected under dark conditions. It has also been proposed (U.S. Pat. No. 787,103 issued Apr. 11, 1905) to apply such light-absorbing colored solutions to a film while it is still in the dark in the camera, or film holder to permit nondark transfer of the film to an ordinary developer solution. In such prior proposals, the filter dye is removed in the course of the usual multisolution processing and washing procedure. It has also been proposed (British Pat. No. 825,146 published Dec. 9, 1959) to perform diffusion transfer processes using processing compositions containing light-absorbing dyes or pigments, e.g., carbon black, to shield the photosensitive stratum from environmental light during processing, both supports being opaque where processing was to be performed in relatively strong light. The processing composition layer containing the light-absorbing dye or pigment was removed with the developed photosensitive material at the end of the processing period to uncover the transfer image. In contrast to these prior art techniques, the present invention makes it possible to retain the optical filter agent

within the final film structure, either in a form which does not exhibit color degrading the image or is effectively masked from view when the image is viewed.

It will be understood that where more than one optical filter agent is employed, their respective color (light-absorbing capacity) may be discharged by different means. Thus, for example, one optical filter agent may be a dye whose color is discharged by a pH change, and that pH-sensitive dye may be used in combination with a dye whose color is discharged by being mordanted behind a reflecting layer. Such combinations of optical filter agents facilitate early viewing of the final image without loss of protection against further exposure, and facilitate the use of optical filter agents present in a precursor form by providing light-absorbing capacity until the precursor has undergone reaction to provide the desired protection (optical density).

It will be recognized that physically removable opaque layers, e.g., pressure-sensitive opaque materials, may be used in combination with an optical filter agent retained in the final film unit with its color discharged. Thus, in the embodiment shown in FIG. 11 one may replace the colorless layer 60 containing an alkali-activated optical filter agent with an opaque stratum removably attached, e.g., by a pressure-sensitive adhesive, to the outer surface of the transparent support 24.

It has previously been noted that the optical filter agent may be rendered nondiffusible by use of suitable long-chain substituents or "ballast" groups. It will be understood that the optical filter agent may also be rendered nondiffusible by being made part of a polymer.

The pH-sensitive optical filter dyes identified above as compounds 13 through 78 are the subject matter of the copending application of Myron S. Simon and David P. Waller, Ser. No. 103,392 filed Jan. 4, 1971, while compounds 79 through 207 are the subject matter of the copending application of Stanley M. Bloom, Alan L. Borrer, Paul S. Huyffer and Paul T. MacGregor, Ser. No. 108,260 filed Jan. 21, 1971.

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 diffusion transfer process comprising photoexposing a photosensitive element including a silver halide emulsion, applying a processing composition thereto to form a laminate including said photoexposed silver halide emulsion, an image-receiving layer, a transparent element and a processing composition permeable light-reflecting layer, said laminate being maintained during and after transfer image formation, developing said photoexposed silver halide emulsion and forming, as a function of said development, a diffusion transfer image in said image-receiving layer, said process being performed in the presence of an organic light-absorptive opacifying agent so positioned in said laminate as to provide a light-absorbing barrier between said transparent element and said photoexposed silver halide emulsion during at least the early stage of said transfer image formation to prevent appreciable further exposure of said photoexposed silver halide emulsion by light passing through said transparent element, said organic light-absorptive opacifying agent being initially positioned in a layer through which said photoexposure is effected, said layer having a pH at which said organic light-absorptive opacifying agent absorbs substantially no visible light by which said silver halide emulsion is exposable, the application of said processing composition providing a pH at which said organic light-absorptive opacifying agent absorbs visible light by which said silver halide emulsion is exposable, said organic light-absorptive opacifying agent being rendered ineffective as a light-absorbing barrier between said transparent element and said image-receiving layer at some stage thereafter so that said transfer image may be clearly viewed through said transparent element, said light-reflecting layer being located between said transparent element and said photoexposed silver halide emulsion and being able to mask

said developed silver halide emulsion when said transfer image is viewed through said transparent element.

2. A diffusion transfer process as defined in claim 1 wherein said organic light-absorptive opacifying agent is a phthalein dye.

3. A diffusion transfer process as defined in claim 1, wherein said layer containing said organic light-absorptive opacifying agent is positioned between said light-reflective layer and said transparent element, said organic light-absorptive opacifying agent absorbing substantially no visible light at the final pH of said laminate.

4. A diffusion transfer process as defined in claim 1, wherein said layer containing said organic light-absorptive opacifying agent is positioned between said light-reflective layer and said photoexposed silver halide emulsion.

5. A diffusion transfer process as defined in claim 1 wherein said transfer image is formed by imagewise transfer of a dye developer.

6. A diffusion transfer process as defined in claim 1, wherein titanium dioxide is present in the processing composition applied to initiate said process, and said light-reflecting layer is formed by solidification of the applied processing composition.

7. A diffusion transfer process comprising photoexposing a photosensitive element including a silver halide emulsion, applying a processing composition thereto to form a laminate including said photoexposed silver halide emulsion, an image-receiving layer, a transparent element and a processing composition permeable light-reflecting layer, said laminate being maintained during and after transfer image formation, developing said photoexposed silver halide emulsion and forming, as a function of said development, a diffusion transfer image in said image-receiving layer, said process being performed in the presence of an organic light-absorptive opacifying agent so constituted and so positioned in said laminate as to provide a light-absorbing barrier between said transparent element and said photoexposed silver halide emulsion during at least the early stage of said transfer image formation to prevent appreciable further exposure of said photoexposed silver halide emulsion by light passing through said transparent element, said organic light-absorptive opacifying agent being rendered ineffective as a light-absorbing barrier between said transparent element and said image-receiving layer at some stage thereafter so that said transfer image may be clearly viewed through said transparent element, said light-reflecting layer being located between said transparent element and said photoexposed silver halide emulsion and being able to mask said developed silver halide emulsion when said transfer image is viewed through said transparent element.

8. A process as defined in claim 7 wherein said light-absorbing reagent is a dye which is colored at the pH at which said first stage of said transfer image formation is performed.

9. A process as defined in claim 8, wherein said dye is present in the processing composition applied to initiate said process.

10. A process as defined in claim 9, wherein said dye becomes mordanted in a layer of said laminate positioned on the opposite side of said light-reflecting layer from said image-receiving layer.

11. A process as defined in claim 8, wherein said dye exhibits light absorption substantially outside of the visible region at a second pH which is lower than said first-mentioned pH.

12. A process as defined in claim 11, wherein said second pH is obtained by the pH-reducing action of an acid-reacting reagent positioned within said laminate, said pH reduction occurring after formation of said transfer image has been completed.

13. A process as defined in claim 12, wherein said acid-reacting reagent is a polymeric acid positioned in a layer between said image-receiving layer and said transparent element.

14. A process as defined in claim 7, wherein said light-reflecting layer comprises titanium dioxide.

15. A process as defined in claim 14, wherein said titanium dioxide is present in the processing composition applied to initiate said process, said processing composition also including a film-forming polymer, and said light-reflecting layer is formed by solidification of the applied processing composition.

16. A diffusion transfer process as defined in claim 7 wherein transfer image comprises a dye released for transfer as the result of a coupling reaction between an oxidized silver halide developing agent and a coupling dye.

17. A diffusion transfer process as defined in claim 7 wherein said transfer image is formed by the diffusion transfer of unoxidized dye developer from said silver halide emulsion to said image-receiving layer.

18. A diffusion transfer process as defined in claim 7 wherein said organic light-absorptive opacifying agent is a phthalein dye.

19. A diffusion transfer process comprising providing a film unit including a first support and a second support, a silver halide emulsion carried on said first support and an image-receiving layer carried on said second support, said second support and the layers between it and said silver halide emulsion being transparent to radiation actinic to said silver halide emulsion; photoexposing said silver halide emulsion through said transparent second support; applying a processing composition between said image-receiving layer and said photosensitive layer, said processing composition including a light-reflecting pigment in a concentration effective to mask said photosensitive layer when said image-receiving layer is viewed through said transparent support; developing said photoexposed silver halide emulsion and forming, as a function of said development, an imagewise distribution of image-forming components which are transferred by diffusion to said image-receiving layer to provide a transfer image viewable through said transparent support without separation of said supports; said film unit further including an organic light-absorptive opacifying agent so positioned between said supports during processing and present in a concentration effective in combination with said pigment to substantially prevent further exposure of said silver halide emulsion during the performance of said transfer process in an area of light actinic to said silver halide emulsion, said opacifying agent being rendered ineffective to prevent viewing of the transfer image against a white background provided by said reflective pigment after completion of said process.

20. A diffusion transfer process as defined in claim 19 wherein said organic light-absorptive opacifying agent is a dye which is light-absorptive at the pH of said processing composition and wherein said dye is rendered non-light-absorptive by the pH reducing action of a polymeric acid after said development has been substantially completed and formation of said transfer image has been substantially completed.

21. A diffusion transfer process as defined in claim 19 wherein said diffusible image-forming component is a dye developer.

22. A diffusion transfer process as defined in claim 19 wherein said diffusible image-forming component is a dye released for transfer as the result of a coupling reaction between an oxidized silver halide developing agent and a coupling dye.

23. A diffusion transfer process as defined in claim 19 wherein said organic light-absorptive opacifying agent and said light-reflective pigment each are present in concentrations which together provide a transmission density greater than 6.0.

24. A diffusion transfer process as defined in claim 19 wherein said organic light-absorptive opacifying agent and said light-reflective pigment each are present in concentrations which together provide a transmission density greater than 7.0.

25. A diffusion transfer process as defined in claim 23 wherein said organic light-absorptive opacifying agent and said light-reflective pigments are present in the same layer.

26. A diffusion transfer process as defined in claim 25 wherein said organic light-absorptive opacifying agent is a dye which is light absorptive at the pH of said processing composition and wherein said dye is rendered non-light-absorptive by the pH-reducing action of a polymeric acid, initially present in said film unit, after said development has been substantially completed.

27. A diffusion transfer process as defined in claim 19, wherein said first support carries a blue-sensitive silver halide emulsion, a green-sensitive silver halide emulsion, and a red-sensitive silver halide emulsion, said silver halide emulsions having associated therewith, respectively, a yellow dye developer, a magenta dye developer and a cyan dye developer, and said transfer image is a multicolor image.

28. A process as defined in claim 27 wherein said red-sensitive silver halide emulsion, said green-sensitive silver halide emulsion and said blue-sensitive silver halide emulsion each are present as separate coplanar layers on said first support.

29. A process as defined in claim 27 wherein said red-sensitive silver halide emulsion, said green-sensitive silver halide emulsion and said blue-sensitive silver halide emulsion are present in the form of minute elements arranged in side-by-side relationship in a photosensitive screen pattern on said first support.

30. A diffusion transfer process as defined in claim 27, wherein said processing composition includes a mixture of organic light-absorptive opacifying agents each of which is a phthalein dye, each said phthalein dye being light-absorptive at the pH of said processing composition thereby providing absorption of light in the visible and near-visible by which said silver halide emulsions are exposable, each said phthalein dye exhibiting light absorption substantially outside of the visible region at a second and lower pH after a predetermined processing period.

31. A diffusion transfer process as defined in claim 19, wherein said light-reflective pigment is titanium dioxide, said organic light-absorptive opacifying agent is a dye which is light-absorptive at the pH of said processing composition and is rendered non-light-absorptive by a reduction in said pH during said process, said pigment and said dye being present in concentrations effective to provide a transmission density of about 6.0.

32. A diffusion transfer process as defined in claim 31 wherein said pH reduction is effected by a polymeric acid positioned in a layer positioned between said image-receiving layer and said transparent second support.

33. In a photographic process wherein a photosensitive element comprising a support carrying a layer of a photosensitive material is exposed imagewise and said exposed photosensitive material is exposed imagewise and said exposed photosensitive material is treated with a processing composition distributed between said support and a second support to provide a visible image, at least one of said supports being transparent to light actinic to said photosensitive material and at least a portion of said treatment being effected in the presence of light actinic to said photosensitive layer, the improvement wherein the application of said processing composition provides a light-absorbing material effective to absorb light passing through said transparent support and actinic to said photosensitive material thereby preventing any substantial increase in the minimum density of the image in said photosensitive layer as a result of a said light being incident on said transparent support during processing of said imagewise exposed photosensitive material, and the light-absorbing capacity of said light-absorbing material is thereafter discharged to permit viewing through said transparent support of the visible image resulting from processing with said processing composition, said discharged light-absorbing material being substantially colorless and retained in the element containing said visible image.

34. A photographic process comprising the steps of selectively exposing a photosensitive element comprising a layer of photosensitive material to radiation actinic thereto to provide

a latent image therein, applying after said exposure a processing composition to provide an optical filter agent in a form capable of absorbing a predetermined wavelength range of said radiation actinic to said photosensitive material, and developing said latent image while exposing said photosensitive element nonselectively to incident actinic radiation within said predetermined wavelength range, said optical filter agent being present during said development in a position and quantity effective to absorb said predetermined wavelength range of incident radiation in an amount sufficient to prevent any substantial increase in the minimum density of the image obtained by said development of said latent image, said optical filter agent being retained in said element in a position and in a substantially colorless form so as to be ineffective to prevent viewing of the final image.

35. A process as defined in claim 34 wherein said photosensitive material is silver halide.

36. A process as defined in claim 35 wherein said silver halide is a direct positive silver halide emulsion.

37. A process as defined in claim 34 wherein said optical filter agent is a dye which is light-absorptive at the pH of said development.

38. A process as defined in claim 37, wherein said dye is substantially colorless at a second pH, and including the step of adjusting the pH of the stratum containing said dye to said second pH.

39. A process as claimed in claim 34 wherein said processing composition is distributed between two strata and confined within a laminate including strata and said layer of photosensitive material.

40. A process as defined in claim 34 wherein said final image is a diffusion transfer image.

41. A process as defined in claim 40 wherein said transfer image is a diffusion transfer image.

42. A process as defined in claim 41 wherein said processing composition is distributed between two strata and confined within a laminate including said strata and said layer of photosensitive material.

43. A process as defined in claim 40 wherein said transfer image is a silver image.

44. A process as defined in claim 40 wherein said transfer image is an additive color image.

45. A process as defined in claim 34 wherein said final image is a negative silver image obtained by development of said latent image.

46. A photographic film unit which comprises a plurality of sequential layers including a layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material which is processing composition soluble and diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive solubilized image-forming material diffusing thereto; means for interposing, intermediate the silver halide layer and the reception layer, an inorganic reflecting pigment dispersion and at least one optical filter agent at a pH above the pKa of the optical filter agent in a concentration effective to provide a layer exhibiting optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to the photosensitive silver halide layer and optical reflection density $< \sim 1.0$ density units with respect to incident visible radiation; and means for reducing the pH of the film unit to a pH below the pKa of the optical filter agent.

47. A photographic film unit as defined in claim 46 wherein the means for interposing the inorganic light-reflecting pigment dispersion comprises providing a processing composition permeable layer, intermediate the silver halide layer and the reception layer, which includes an inorganic light-reflecting pigment dispersion containing at least one pH-sensitive dye at a pH below the pKa of the dye in a concentration effective upon contact with a processing composition possessing a pH above the pKa of the dye to provide a layer exhibiting optical transmission density $> \sim 6.0$ density units and optical reflection density $< \sim 1.0$ density units.

48. A photographic film unit as defined in claim 46 wherein the means for interposing said inorganic light-reflecting pigment dispersion comprises means for introducing a photographic processing composition, intermediate the silver halide layer and the reception layer, which includes an inorganic light-reflecting pigment dispersion and at least one pH-sensitive dye at a pH above the pKa of the dye, to provide a layer exhibiting the optical transmission density $> \sim 6.0$ density units and the optical reflection density $< \sim 1.0$ density units.

49. A photographic film unit as defined in claim 48 wherein the means for introducing the photographic processing composition comprises a rupturable container retaining the processing composition positioned extending transverse an edge of the film unit to effect, upon application of compressive pressure to the container, discharge of the container's processing composition contents intermediate the silver halide layer and the reception layer.

50. A photographic film unit as defined in claim 49 wherein the image-forming material is a dye image-forming material.

51. A photographic film unit as defined in claim 50 wherein the dye image-forming material comprises a dye which is a silver halide developing agent.

52. A photographic film unit as defined in claim 51 including, intermediate the opaque layer and the reception layer, at least two selectively sensitized silver halide emulsion layers each having a dye which dye is a silver halide developing agent of predetermined color associated therewith, each of the dyes soluble and diffusible in processing composition possessing a pH above the pKa of the pH sensitive dye as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

53. A photographic film unit as defined in claim 52 wherein each of the selectively sensitized silver halide emulsion layers possesses predominant spectral sensitivity to separate regions of the spectrum and the dye associated with each of said silver halide emulsion layers possesses a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity image of its associated emulsion layer.

54. A photographic film unit as defined in claim 53 wherein at least one optical filter agent exhibits, at a pH above its pKa, major spectral absorption in the spectral region within which a selectively sensitized silver halide emulsion layer possesses predominant spectral sensitivity.

55. A photographic film unit as defined in claim 46 wherein the pH above the pKa of the filter agent is an alkaline pH.

56. A photographic film unit as defined in claim 55 wherein the dye image-forming material comprises a dye which is a silver halide developing agent soluble and diffusible in aqueous alkaline solution at a first pH above the pKa of the filter agent and substantially nondiffusible at a second pH below the pKa of the filter agent.

57. A photographic film unit as defined in claim 56 including at least one acid layer positioned in film unit and adapted to reduce the pH of an aqueous alkaline processing solution possessing a first pH above the pKa of the filter agent at which the dye is soluble and diffusible to a second pH below the pKa of the filter agent at which the dye is substantially nondiffusible subsequent to substantial transfer of dye to the reception layer.

58. A photographic film unit as defined in claim 56 wherein the inorganic light-reflecting pigment titanium dioxide.

59. A photographic film unit as defined in claim 58 wherein the optical filter agent comprises a phthalein pH-sensitive dye possessing a pKa below the first pH and above the second pH.

60. A photographic film unit as defined in claim 59 wherein the pH-sensitive dye is substantially nondiffusible from the inorganic light-reflecting pigment dispersion.

61. A photographic film unit as defined in claim 46 wherein said solubilized image-forming material is a dye released for transfer as the result of the reaction of an oxidized silver halide developing agent.

62. A photographic film unit adapted to be processed by passing the unit between a pair of juxtaposed pressure-applying members and which comprises, in combination:

a photosensitive element including a composition structure containing, as essential layers, a dimensionally stable opaque layer; at least two selectively sensitized silver halide emulsions layers possessing predominant spectral sensitivity to separate regions of the visible electromagnetic spectrum and a dye which is a silver halide developing agent and is soluble and diffusible, in alkaline processing composition, at a first pH associated with each of the silver halide emulsion layers and possessing a spectral absorption range subsequent to processing substantially complementary to the predominant sensitivity range of its associated emulsion layer; an alkaline solution permeable and dyeable polymeric layer; a polymeric layer possessing acid capacity effective to reduce alkaline processing composition possessing the first pH to a second pH at which the dyes are substantially nondiffusible; a dimensionally stable transparent layer; and means securing the layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing composition possessing the first pH and retaining substantially uniformly disposed therein titanium dioxide and optical filter agent substantially nondiffusible from the processing composition and possessing a pKa below the first pH and above the second pH wherein the filter agent exhibits spectral absorption substantially complementary to the predominant sensitivity range of the selectively sensitized silver halide emulsion layers at the first pH and the titanium dioxide and filter agent are present in a quantity sufficient, upon distribution of the alkaline processing composition possessing the first pH as a layer intermediate the dyeable polymeric layer and next adjacent selectively sensitized silver halide emulsion layer, to provide to the layer an optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to the silver halide emulsion layers and an optical reflection $< \sim 1.0$ density units with respect to incident visible radiation, and said rupturable container is positioned and extends transverse an edge of the photosensitive element to effect unidirectional discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the selectively sensitized silver halide emulsion layer next adjacent.

63. A photographic film unit as defined in claim 62 wherein the silver halide is present in a concentration within the image of ~ 125 to 500 mg./ft.².

64. A photographic film unit as defined in claim 63 wherein the titanium dioxide is distributed intermediate the dyeable polymeric layer and the silver halide emulsion layer next adjacent at a coverage within the range of $\sim 1,500$ to $4,000$ mg./ft.².

65. A photographic film unit adapted to be processed by passing said unit 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 dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each of the cyan, magenta and yellow dyes being silver halide developing agents and being soluble and diffusible, in alkali, at a first pH; an alkaline solution permeable and dyeable polymeric layer; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition having the first pH to a second pH at which the dyes are substantially nondiffusible; a dimensionally stable alkaline solution impermeable transparent layer; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition having the first pH and containing substantially uniformly dispersed therein titanium

dioxide and at least three pH-sensitive dyes substantially nondiffusible from such processing composition and possessing a pKa below the first pH and above the second pH thereby exhibiting major spectral absorption at said first pH and minor spectral absorption at said second pH, at least one of the pH-sensitive dyes possessing predominant spectral absorption in the blue region of the electromagnetic spectrum to which the blue-sensitive emulsion is sensitive, at least one of the pH-sensitive dyes possessing predominant spectral absorption in the green region of the electromagnetic spectrum to which the green-sensitive emulsion is sensitive and at least one of the pH-sensitive dyes possessing predominant spectral absorption in the red region of the electromagnetic spectrum to which the red-sensitive emulsion is sensitive, the titanium dioxide and the pH-sensitive dyes taken together present in a quantity sufficient, upon distribution of the aqueous alkaline processing composition possessing the first pH as a layer, intermediate the dyeable polymeric layer and the blue-sensitive silver halide emulsion layer, to provide to the layer an optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic the silver halide emulsion layers and an optical reflection density $< \sim 1.0$ density units with respect to incident visible radiation, said container fixedly positioned and extending transverse an edge of the photosensitive element to effect unidirectional discharge of the container's aqueous alkaline processing composition possessing the first pH intermediate the dyeable polymeric layer and the blue-sensitive silver halide emulsion layer.

66. A photographic film unit which comprises a plurality of sequential layers including a layer transparent to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material which is processing composition soluble and diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation through said transparent layer; a layer adapted to receive solubilized image-forming material diffusing thereto; means for interposing, intermediate the silver halide layer and the reception layer, at least one optical filter agent in a concentration effective to provide a layer exhibiting optical transmission density with respect to incident radiation actinic to the photosensitive silver halide layer effective to shield said silver halide from actinic radiation incident upon said transparent layer after photoexposure, and means for discharging the color of said optical filter agent, subsequent to substantial diffusion of solubilized image-forming material to the layer adapted to receive image-forming material diffusing thereto, without removing said optical filter agent from said film unit.

67. A photographic film unit as defined in claim 66 including a layer opaque to incident actinic radiation.

68. A photographic film unit as defined in claim 66 including means for interposing, between said silver halide layer and said receiving layer, an inorganic light-reflecting pigment dispersion.

69. A photographic film unit as defined in claim 66 wherein said optical filter agent is a pH-sensitive dye and said means for discharging the color of said optical filter agent comprises an acid positioned in a layer of said film unit.

70. A photographic film unit as defined in claim 69 including a polymeric layer positioned between said acid-containing layer and said optical filter agent and adapted to substantially prevent reaction of said acid with alkali for a predetermined time.

71. A photographic film unit as defined in claim 69 wherein said acid is a polymeric acid.

72. A photographic film unit as defined in claim 66 including means for interposing an inorganic light-reflecting white pigment dispersion between said silver halide and said receiving layer, said optical filter agent is a dye, and said means for discharging the color of said optical filter agent comprising a mordant for said optical filter agent so positioned with respect to said receiving layer as to be masked by said pigment dispersion.

73. A photographic film unit as defined in claim 66 wherein said optical filter agent is initially positioned in a layer of said film unit in the form of a substantially colorless precursor which provides said optical filter agent by interaction with a component of said processing composition.

74. A photographic film unit as defined in claim 73 wherein said optical filter agent is a substantially nondiffusible pH-sensitive dye initially present in said film unit at a pH below its pKa.

75. A process for providing a photographic diffusion transfer image which comprises, in combination, the steps of:

- a. exposing to incident electromagnetic radiation a photographic film unit which comprises a plurality of sequential layers including a layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material which is processing composition soluble and diffusible as a function of the point-to-point degree of silver halide layer exposure to incident actinic radiation; a layer adapted to receive solubilized image-forming material diffusing thereto; means for interposing, intermediate the silver halide layer and the reception layer, an inorganic reflecting pigment dispersion containing at least one optical filter agent at a pH above the pKa of the optical filter agent in a concentration effective to provide a layer exhibiting optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to the photosensitive silver halide layer and optical reflection density $< \sim 1.0$ density units with respect to incident visible radiation; and means for reducing the pH of the film unit to a pH below the pKa of the optical filter agent;
- b. interposing the inorganic reflecting pigment dispersion intermediate the silver halide layer and the reception layer;
- c. contacting the photoexposed silver halide layer with a processing composition adapted to effect development of the silver halide layer;
- d. effecting thereby development of the photoexposed silver halide layer;
- e. forming thereby an imagewise distribution of mobile image-forming material as a function of the point-to-point degree of silver halide layer photoexposure;
- f. transferring, by diffusion, at least a portion of the imagewise distribution of mobile image-forming material to the layer adapted to receive image-forming material diffusing thereto to thereby provide an image in terms of the imagewise distribution; and
- g. reducing the pH of the film unit to a pH below the pKa of the optical filter agent.

76. A process for providing a photographic diffusion transfer image as defined in claim 75 wherein the means for interposing the inorganic light-reflecting pigment dispersion comprising including within the photographic film unit, intermediate the silver halide layer and the reception layer, a preformed processing composition permeable layer which includes an inorganic light-reflecting pigment dispersion containing at least one pH-sensitive dye at a pH below the pKa of the dye and a concentration effective upon contact with a processing composition possessing a pH above the pKa of the dye to provide a layer exhibiting the optical transmission density $> \sim 6.0$ density units and the optical reflection density $< \sim 1.0$ density units, and including the step of contacting the pH-sensitive dye, subsequent to photoexposure of the film unit, with a processing composition possessing a pH above the pKa of the dye to provide a layer exhibiting the optical transmission density $> \sim 6.0$ density units and the optical reflection density $< \sim 1.0$ density units.

77. A process for providing a photographic diffusion transfer image as defined in claim 75 wherein the processing composition adapted to effect development of the silver halide layer includes the inorganic light-reflecting pigment dispersion containing at least one pH-sensitive dye at a pH above the pKa of the dye, and including the step of interposing the processing composition, intermediate the silver halide layer

and the reception layer, subsequent to photoexposure of the silver halide layer, to provide a layer exhibiting the optical transmission density $> \sim 6.0$ density units and the optical reflection density $< \sim 1.0$ density units.

78. A process for providing a photographic diffusion transfer image as defined in claim 75 wherein the image-forming material is a dye image-forming material.

79. A process for providing a photographic diffusion transfer image as defined in claim 78 wherein the dye image-forming material comprises a dye which is a silver halide developing agent.

80. A process for providing a photographic diffusion transfer image as defined in claim 79 wherein the dye which is a silver halide developing agent is soluble and diffusible in aqueous alkaline processing composition at a first pH above the pKa of the pH-sensitive dye and substantially nondiffusible at a second pH below the pKa of the pH-sensitive dye.

81. A process for providing a photographic diffusion transfer image in color as defined in claim 80 wherein the photographic film unit includes a layer adapted to reduce the pH of the film unit from the first pH to the second pH subsequent to substantial dye transfer image formation in the layer adapted to receive solubilized image dye diffusing thereto, and including the step of diffusing, subsequent to substantial dye transfer image formation, a sufficient portion of the ions of the alkaline processing composition to the layer adapted to reduce the pH of the film unit to thereby reduce the alkalinity of the film unit from the first pH to the second pH.

82. A process for providing a multicolored diffusion transfer image which comprises, in combination, the steps of:

a. exposing to incident actinic radiation a composite photographic film unit which comprises a plurality of sequential layers including a dimensionally stable layer opaque to incident actinic radiation; at least two selectively sensitized silver halide emulsion layers possessing predominant spectral sensitivity to separate regions of the visible electromagnetic spectrum and a dye which is a silver halide developing agent and is soluble and diffusible in aqueous alkaline processing composition, at a first pH, associated with each of the silver halide emulsion layers and possessing spectral absorption range, subsequent to processing, substantially complementary to the predominant sensitivity range of its associated silver halide emulsion layers; an alkaline solution dyeable polymeric layer; a dimensionally stable layer transparent to incident actinic radiation; at least one layer possessing neutralizing capacity effective to reduce the alkaline processing composition possessing the first pH to a second pH at which the dyes are substantially nondiffusible positioned intermediate at least one of the dimensionally stable opaque or transparent layers and next adjacent essential layer; and means of securing the layers in substantially fixed relationship;

a rupturable container retaining an alkaline processing composition possessing the first pH and retaining substantially uniformly dispersed therein an inorganic light-reflecting pigment and at least one optical filter agent, substantially nondiffusible from the processing composition and possessing a pKa below the first pH and above the second pH, exhibiting spectral absorption substantially complementary to the predominant sensitivity range of the selectively sensitized silver halide emulsion layers, at the first pH, and the light-reflecting pigment and optical filter agent are present in a quantity sufficient, upon distribution of the alkaline processing composition possessing the first pH as a layer intermediate the dyeable polymeric layer and next adjacent selectively sensitized silver halide emulsion layer, to provide a layer exhibiting an optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to the silver halide emulsion layers and an optical reflection density $< \sim 1.0$ density units with respect to visible radiation, and the rup-

turable container is positioned and extends transverse an edge of the photosensitive element to effect discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the selectively sensitized silver halide emulsion layer next adjacent;

b. effecting discharge of the container's alkaline processing composition intermediate the dyeable polymeric layer and the photosensitive silver halide emulsion layer next adjacent;

c. effecting thereby development of each of the silver halide emulsions;

d. immobilizing the dye associated with each of the silver halide emulsions as a function of the point-to-point degree of exposure thereof;

e. forming thereby an imagewise distribution of mobile dye as a function of development;

f. transferring, by diffusion, at least a portion of each of the imagewise distributions of mobile dye to the dyeable polymeric layer to provide thereto a dye image in terms of the imagewise distributions;

g. transferring, by diffusion, subsequent to substantial dye transfer image formation, a sufficient portion of the ions of the alkaline processing composition to the neutralizing layer to thereby reduce the alkalinity of the composition from the first pH at which the dyes associated with the silver halide emulsions are soluble and diffusible and above the pKa of the pH-sensitive dye to the second pH below the pKa of the pH-sensitive dye and at which the dyes associated with the silver halide emulsions are substantially nondiffusible; and

h. maintaining the composite structure intact subsequent to processing.

83. A process for providing a photographic diffusion transfer multicolor image which comprises, in combination, the steps of:

a. exposing to incident actinic radiation a photographic film unit which comprises a composite structure containing, as essential layers, in sequence, a dimensionally stable alkaline solution impermeable opaque layer; a red-sensitive silver halide emulsion layer having associated therewith cyan dye; a green-sensitive silver halide emulsion layer having associated therewith magenta dye; a blue-sensitive silver halide emulsion layer having associated therewith yellow dye, each the cyan, magenta, and yellow dyes being soluble and diffusible, in alkali, at a first pH; an alkaline solution permeable and dyeable polymeric layer; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition having the first pH at which the cyan, magenta and yellow dyes are soluble and diffusible to a second pH at which the dyes are substantially nondiffusible; a dimensionally stable alkaline solution impermeable transparent layer; and means securing said layers in substantially fixed relationship; and

a rupturable container retaining an aqueous alkaline processing composition having the first pH and containing substantially uniformly dispersed therein titanium dioxide and at least three pH-sensitive phthalein dyes substantially nondiffusible from said processing composition and possessing a pKa below the first pH and above the second pH, at least one of the pH-sensitive dyes possessing predominant spectral absorption in the blue region of the electromagnetic spectrum to which the blue-sensitive silver halide emulsion is sensitive, at least one of the pH-sensitive dyes possessing predominant spectral absorption in the green region of the electromagnetic spectrum to which the green-sensitive silver halide emulsion is sensitive, and at least one of the pH-sensitive dyes possessing predominant spectral absorption red region of the electromagnetic region of the spectrum to which the red-sensitive silver halide emulsion is sensitive, the titanium dioxide and the pH-sensitive dyes taken together being present in a quantity sufficient, upon distribution of the

aqueous alkaline processing composition possessing the first pH as a layer intermediate the dyeable polymeric layer and the blue-sensitive silver halide emulsion layer, to provide a layer possessing an optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to the silver halide emulsion layers and an optical reflection density $< \sim 1.0$ density units with respect to incident visible radiation, and the container is fixedly positioned and extends transverse a leading edge of the photosensitive element to effect upon application of compressive force unidirectional discharge of the container's aqueous alkaline processing composition possessing the first pH intermediate the dyeable polymeric layer and blue-sensitive silver halide emulsion layer;

- b. applying compressive force to the rupturable container to effect unidirectional discharge of the container's aqueous alkaline processing composition intermediate the dyeable polymeric layer and the blue-sensitive silver halide layer;
- c. effecting thereby development of the red, green and blue sensitive silver halide emulsion;
- d. immobilizing the cyan, magenta and yellow dyes as a result of development of their associated silver halide emulsion;
- e. forming thereby an imagewise distribution of mobile cyan, magenta and yellow dye as a function of the point-to-point degree of exposure of their associated silver halide emulsion;
- f. transferring, by diffusion, at least a portion of each of the imagewise distributions of mobile cyan, magenta and yellow dye to the alkaline solution permeable polymeric layer dyeable by said dyes to provide thereto a multicolor dye image;
- g. transferring, by diffusion, subsequent to substantial dye transfer, a sufficient portion of the ions of the aqueous alkaline processing composition to the polymeric acid layer to thereby reduce the alkalinity of the film unit from the first pH, above the pKa of the pH-sensitive dyes, at which the cyan, magenta and yellow image dyes are soluble and diffusible to a second pH, below the pKa of the pH-sensitive dyes, at which the cyan, magenta and yellow image dyes are substantially nondiffusible; and
- h. maintaining the composite structure intact subsequent to processing.

84. A process for providing a photographic diffusion transfer multicolor image as defined in claim 83 wherein the titanium dioxide is distributed intermediate the dyeable polymeric layer and the blue-sensitive silver halide emulsion layer at a coverage within the range of 1,500 to 4,000 mg./ft.².

85. A process for providing a photographic diffusion transfer multicolor image as defined in claim 83 wherein said optical filter agent possesses a pKa $> \sim 12$.

86. A process for providing a photographic diffusion transfer image which comprises, in combination, the steps of:

- a. exposing to incident electromagnetic radiation a photographic film unit which comprises a plurality of sequential layers including a layer transparent to incident actinic radiation; a photosensitive silver halide layer having associated therewith image-forming material adapted to provide an imagewise distribution of a processing composition soluble and diffusible image-forming material as a function to the point-to-point degree of silver halide layer exposure to incident actinic radiation through such transparent layer; a layer adapted to receive solubilized image-forming material diffusing thereto; means for interposing, intermediate the silver halide layer and the reception layer, at least one optical filter agent in a concentration effective to provide a layer exhibiting optical transmission density with respect to incident radiation actinic to the photosensitive silver halide layer effective to shield said silver halide from actinic radiation incident upon said transparent layer after photoexposure; and means for discharging the color of said optical filter agent, without removing said optical filter agent from said film unit, sub-

sequent to substantial diffusion of solubilized image-forming material to the layer adapted to receive image-forming material diffusing thereto;

- b. interposing said optical filter agent in a light-absorbing form intermediate said silver halide layer and said reception layer;
- c. contacting the photoexposed silver halide layer with a processing composition adapted to effect development of the silver halide layer;
- d. effecting thereby development of the photoexposed silver halide layer;
- e. forming thereby an imagewise distribution of diffusible image-forming material as a function of the point-to-point degree of silver halide layer photoexposure;
- f. transferring, by diffusion, at least a portion of the imagewise distribution of diffusible image-forming material to the layer adapted to receive image-forming material diffusing thereto to thereby provide an image in terms of the imagewise distribution; and
- g. discharging, subsequent to substantial transfer of said diffusible image-forming material to said reception layer, said optical filter agent.

87. A photographic process as defined in claim 86 wherein said film unit includes a layer opaque to said incident actinic radiation.

88. A photographic process as defined in claim 86 wherein said film unit includes a second optical filter agent positioned in a layer on the opposite side of said silver halide emulsion from said receiving layer.

89. A photographic process as defined in claim 88 including the step of discharging said second optical filter agent subsequent to said diffusion transfer of image-forming material.

90. A photographic process as defined in claim 86 wherein an inorganic light-reflecting white pigment dispersion is provided intermediate said silver halide layer and said receiving layer.

91. A photographic process as defined in claim 90 wherein said pigment is included in said processing composition.

92. A photographic process as defined in claim 86 wherein said optical filter agent is a pH-sensitive dye and the color thereof is discharged by the reaction of alkali with an acid positioned in a layer of said film unit thereby reducing, after a predetermined time, the pH of the layer containing said pH-sensitive dye to a pH below the pKa of said pH-sensitive dye.

93. A photographic process as defined in claim 89 wherein each of said optical filter agents is a pH-sensitive dye and the color thereof is discharged by the reaction of alkali with an acid positioned in a layer of said film unit thereby reducing, after a predetermined time, the pH of each layer containing said pH-sensitive dyes to a pH below the respective pKa of said pH-sensitive dyes.

94. A photographic process as defined in claim 93 wherein said acid is a polymeric acid.

95. A photographic process as defined in claim 93 wherein said film unit includes a polymeric layer positioned between said acid-containing layer and said optical filter agent and adapted to substantially prevent reaction of said acid with alkali for a predetermined time.

96. A photographic process as defined in claim 86 wherein an inorganic light-reflecting white pigment dispersion is provided between said silver halide and said receiving layer, said optical filter agent is a dye initially present in said processing composition, and said dye is discharged by being mordanted in a stratum of said film unit so positioned as to be masked by said white pigment.

97. A photographic process as defined in claim 86 wherein said optical filter agent is initially present as a substantially colorless precursor positioned in a layer of said film unit through which photoexposure is effected, said precursor providing said optical filter agent by interaction with a component of said processing composition.

98. A photographic process as defined in claim 97 wherein said optical filter agent is a pH-sensitive dye initially present in said layer at a pH below its pKa.

99. A photographic film unit comprising a plurality of superposed or superposable layers including a layer of a photosensitive silver halide and at least one outermost layer transparent to incident radiation actinic to said photosensitive silver halide; a layer adapted to contain a visible image formed as a function of development of said photosensitive silver halide and selected from the group consisting of said layer of photosensitive silver halide and a separate, superposed image-carrying layer; means adapted to interpose, intermediate said layer of photosensitive silver halide and said transparent layer and after photoexposure of said photosensitive silver halide, at least one optical filter agent in a concentration effective to provide a layer exhibiting optical transmission density, with respect to radiation actinic to said photosensitive silver halide, effective to shield said silver halide from said actinic radiation incident upon said transparent layer after photoexposure; container means releasably holding a processing composition adapted to effect development of said photosensitive silver halide after photoexposure and to provide said visible image as a function of said development; and means for discharging the color of said optical filter agent to permit viewing said visible image through said transparent layer, subsequent to substantial completion of said development and visible image formation, without removing said optical filter agent from said film unit.

100. A photographic film unit as defined in claim 99, wherein said processing composition includes a white pigment, and said white pigment and said optical filter agent in combination are effective to provide an optical transmission density $> \sim 6.0$ density units with respect to incident radiation actinic to said photosensitive silver halide.

101. A photographic film unit as defined in claim 100, wherein said optical transmission density is $> \sim 7.0$ density units.

102. A photographic film unit as defined in claim 99 wherein said image-containing layer is an image-carrying layer including an image dye or an image dye intermediate adapted to be removed imagewise from said image-carrying layer as a function of said development.

103. A photographic film unit as defined in claim 102 wherein said image-carrying layer includes a nondiffusible dye adapted to be bleached by the silver dye bleach process.

104. A photographic film unit as defined in claim 102 wherein said image-carrying layer includes a nondiffusible dye adapted to provide a diffusible reaction product as a result of coupling with the oxidation product of a silver halide developing agent.

105. A photographic film unit as defined in claim 102 wherein said image-carrying layer includes a nondiffusible dye adapted to provide a diffusible reaction product as a result of oxidation.

106. A photographic film unit as defined in claim 99 wherein said optical filter agent comprises a phthalein dye.

107. A photographic film unit as defined in claim 99 wherein said optical filter agent comprises at least two phthalein dyes.

108. A photographic film unit as defined in claim 99 wherein said optical filter agent is substantially nondiffusible from said layer containing said optical filter agent.

109. A photographic film unit as defined in claim 99 wherein said image-carrying layer is a silver transfer image receiving layer; and a layer containing an additive color screen positioned between said transparent outermost layer and said image-carrying layer.

110. A photographic film unit as defined in claim 99 wherein said optical filter agent is substantially nondiffusible and is initially positioned in a layer through which photoexposure of said silver halide emulsion is effected, said layer having a pH at which said organic light-absorptive opacifying agent absorbs substantially no visible light by which said silver halide emulsion is exposable, said processing composition being effective when distributed to provide a pH at which said organic light-absorptive opacifying agent will absorb visible light by which said silver halide is exposable.

111. A photographic film unit as defined in claim 110, wherein a second optical filter agent is included in said processing composition whereby a layer containing an optical filter agent is positioned on each side of said silver halide layer.

112. A diffusion transfer process film unit including a first support and a second support, a silver halide emulsion carried on said first support, a dye image-providing material positioned in a layer carried on said first support, and an image-receiving layer carried on said second support, said second support and the layers between it and said silver halide emulsion being transparent to radiation actinic to said silver halide emulsion; a processing composition releasably contained in a rupturable container positioned to release said composition for distribution between said image-receiving layer and said photosensitive layer, said processing composition including a light-reflective pigment in a concentration effective to mask said photosensitive layer when said image-receiving layer is viewed through said transparent support; said dye image-providing material being adapted to provide a diffusible image-forming component as a function of said development, said film unit further including an organic light-absorptive opacifying agent adapted to be so positioned between said supports during processing and present in a concentration effective in combination with said pigment to substantially prevent further exposure of said silver halide emulsion during the performance of said transfer process in an area of light actinic to said silver halide emulsion, said opacifying agent being adapted to be rendered ineffective to prevent viewing of the transfer image against a white background provided by said reflective pigment after completion of said process.

113. A diffusion transfer process film unit as defined in claim 112 wherein said organic light-absorptive opacifying agent is a dye which is light absorptive at the pH of said processing composition and wherein said dye is adapted to be rendered non-light-absorptive by the pH-reducing action of a polymeric acid positioned in a layer of said film unit.

114. A diffusion transfer process film unit as defined in claim 112 wherein said diffusible image-forming component is a dye developer.

115. A diffusion transfer process film unit as defined in claim 112 wherein said diffusible image-forming component is a dye released for transfer as the result of a coupling reaction between an oxidized silver halide developing agent and a coupling dye.

116. A diffusion transfer process film unit as defined in claim 112 wherein said organic light-absorptive opacifying agent is initially included in said processing composition.

117. A diffusion transfer process film unit as defined in claim 112 wherein said organic light-absorptive opacifying agent is initially positioned in a layer through which photoexposure of said silver halide emulsion is effected, said layer having a pH at which said organic light-absorptive opacifying agent absorbs substantially no visible light by which said silver halide emulsion is exposable, said processing composition being effective when distributed to provide a pH at which said organic light-absorptive opacifying agent will absorb visible light by which said silver halide emulsion is exposable.

118. A diffusion transfer process film unit as defined in claim 112 wherein said organic light-absorptive opacifying agent is a phthalein dye.

119. A diffusion transfer process film unit as defined in claim 112, wherein said first support carries a blue-sensitive silver halide emulsion, a green-sensitive silver halide emulsion, and a red-sensitive silver halide emulsion, said silver halide emulsions having associated therewith, respectively, a yellow dye developer, a magenta dye developer and a cyan dye developer.

120. A diffusion transfer process film unit as defined in claim 119, wherein said red-sensitive silver halide emulsion, said green-sensitive silver halide emulsion and said blue-sensitive silver halide emulsion each are present as separate coplanar layers on said first support.

121. A diffusion transfer process film unit as defined in

claim 119, wherein said red-sensitive silver halide emulsion, said green-sensitive silver halide emulsion and said blue-sensitive silver halide emulsion are present in the form of minute elements arranged in side-by-side relationship in a photosensitive screen pattern on said first support.

122. A rupturable container releasably holding an aqueous alkaline processing composition for use in diffusion transfer processes including a film-forming, viscosity-providing polymer dissolved therein and an inorganic light-reflecting pigment, said composition also including a dye which absorbs light within the visible region at the pH of said aqueous alkaline composition, said dye exhibiting light absorption substantially outside of the visible region at a second pH which is lower than said first-mentioned pH.

123. A rupturable container releasably holding an aqueous alkaline processing composition as defined in claim 122 wherein said dye is a phthalein dye.

124. A rupturable container releasably holding an aqueous alkaline processing composition as defined in claim 122 wherein said light-reflecting pigment is titanium dioxide.

125. A photographic film unit as defined in claim 118 wherein said layer of photosensitive material is protected from radiation actinic to said photosensitive material and incident upon the surface of said film unit opposite from said optical filter agent layer by a physically removable opaque layer.

126. A photographic film unit as defined in claim 125 wherein said physically removable opaque layer is secured to a transparent layer by a pressure sensitive adhesive.

127. A photographic film unit as defined in claim 66, wherein said film unit includes at least a first and a second optical filter agent, said first optical filter agent being pH sensitive and having its color discharged by a reduction in pH, and said second optical filter agent being a dye whose color is

discharged by being mordanted in a layer behind a light-reflecting layer.

128. A photographic film unit as defined in claim 66 including a development restrainer so positioned in said film unit as to become available to stop development of undeveloped silver halide after a predetermined period.

129. A photographic film unit as defined in claim 128 wherein said development restrainer is positioned in said image reception layer.

130. A photographic film unit as defined in claim 66 including a desensitizing agent to desensitize unexposed silver halide after photoexposure and application of a processing composition.

131. A photographic process as defined in claim 33 wherein said processing composition is providing by impregnating said processing composition into a layer carried by said second support prior to superposing said second support on said photosensitive element.

132. An image-receiving element for use in diffusion transfer processes comprising a transparent support carrying at least a first transparent layer and a second transparent layer, said first transparent layer including a dye mordant and said second transparent layer including a substantially nondiffusible, pH-sensitive dye at a pH below its pKa whereby said pH-sensitive dye is substantially colorless.

133. An image-receiving element as defined in claim 132 including a third transparent layer containing an acid-reacting reagent positioned between said support and said dye mordant containing layer.

134. An image-receiving element as defined in claim 133 wherein said acid reacting reagent is a polymeric acid.

* * * * *

UNITED STATES PATENT OFFICE Page 1
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, lines 15 and 16, "including" should be --include--.

Column 5, line 66, "an" (first occurrence) should be --and--.

Column 6, line 45, "approximately" should be --approximating--.

Column 9, line 52, before "9" insert --pH--.

Column 9, line 68, "for" should be --by--.

Column 15, line 3, after "the" (first occurrence) insert --optical--.

Column 15, line 23, "possible" should be --possibly--.

Column 15, line 56, after "1971" insert --)---.

Column 16, lines 4 and 5, "underdeveloped" should be --undeveloped--.

Column 17, line 3, after "1971" insert --)---.

Column 22, line 63, after "100 mg./ft.²" insert --of gelatin. A green-sensitive gelatino-silver iodobromide₂ emulsion was then coated at a coverage of about 100 mgs./ft.²---.

Column 23, line 11, "583 μ u" should be --593 μ u--.

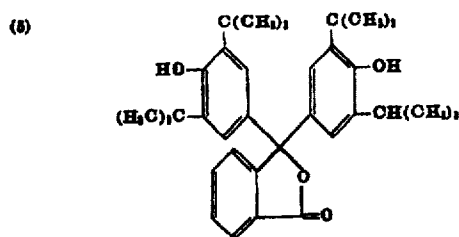
UNITED STATES PATENT OFFICE Page 2
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

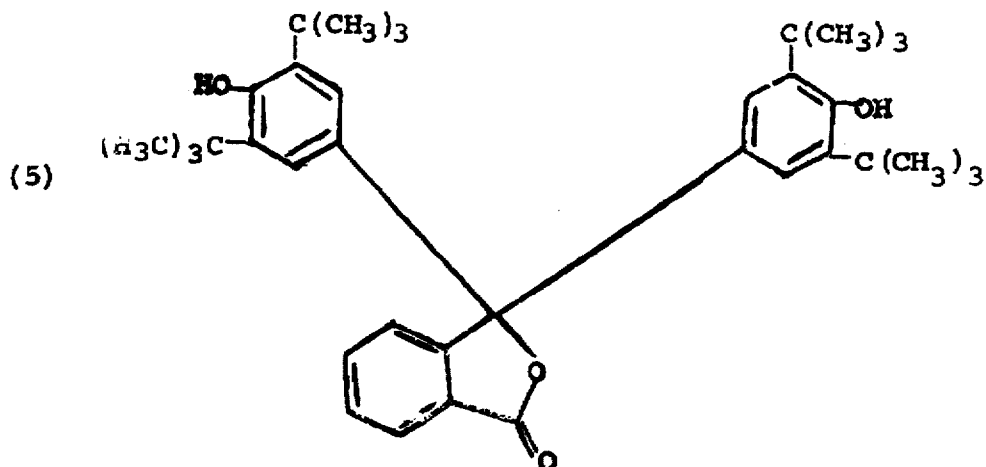
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 24, Formula (5)



should be



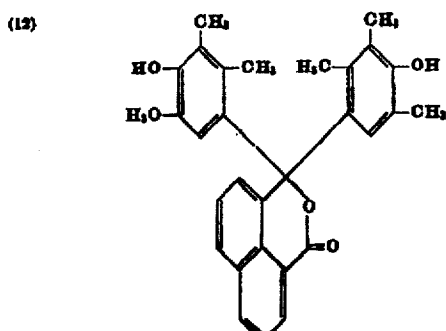
UNITED STATES PATENT OFFICE Page 3
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

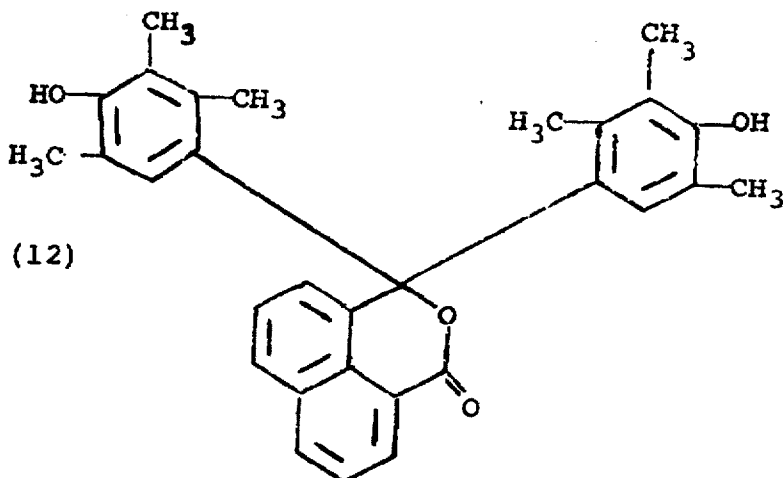
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 25, Formula (12)



should be



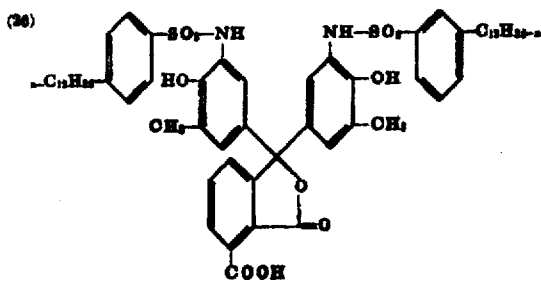
Page 4

Dated March 7, 1972

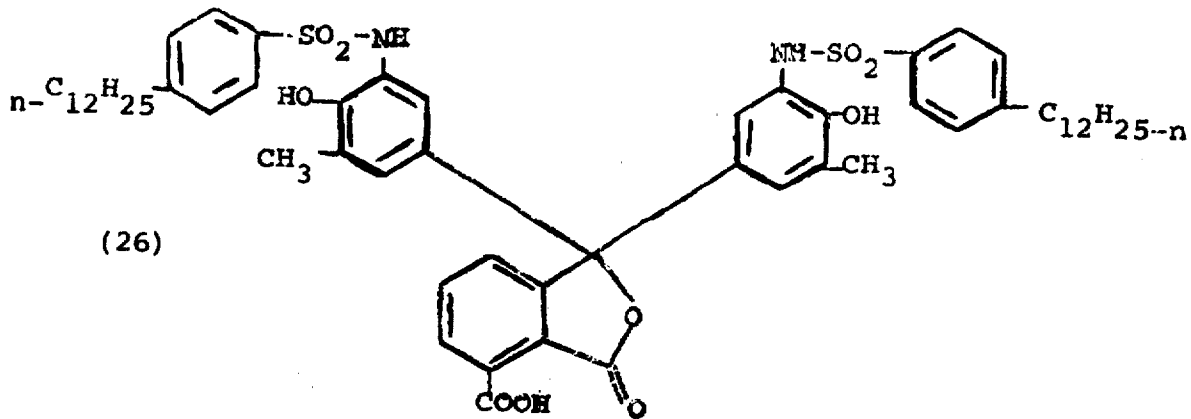
Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 27, Formula (26)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

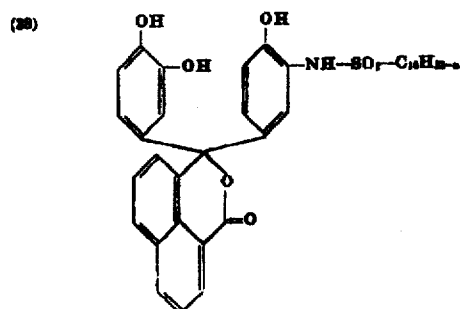
Page 5

Patent No. 3,647,437 Dated March 7, 1972

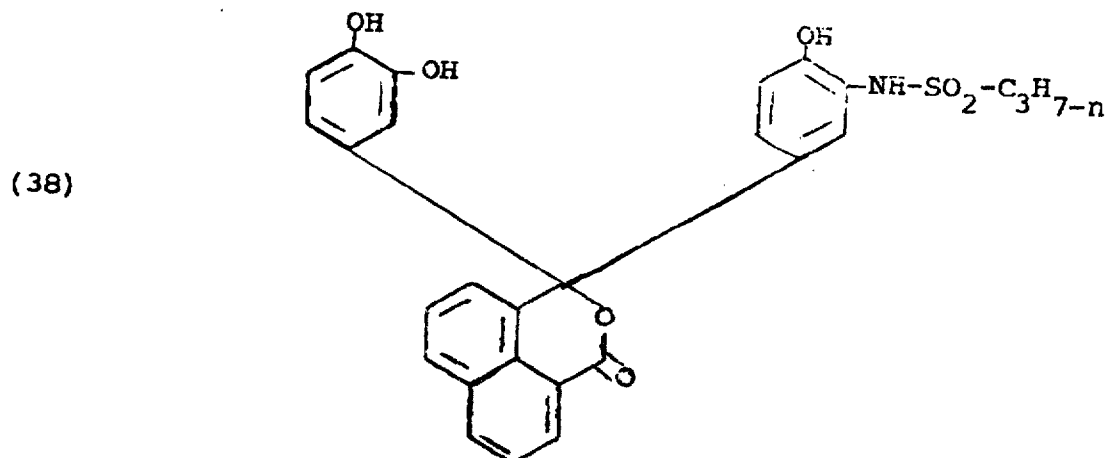
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 29, Formula (38)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

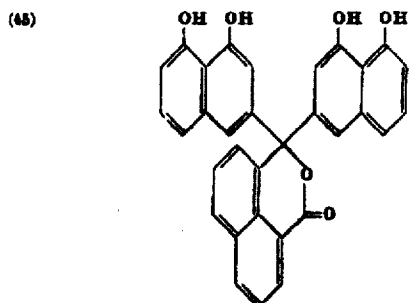
Page 6

Patent No. 3,647,437 Dated March 7, 1972

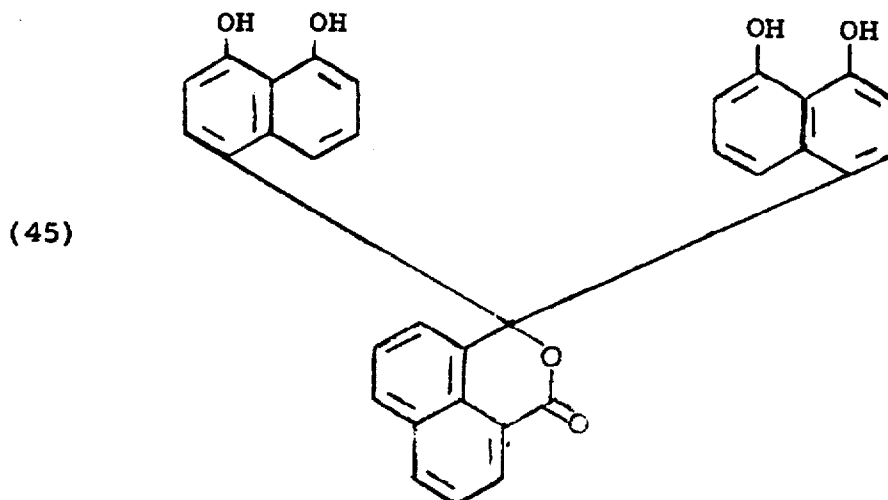
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Column 31, Formula (45)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

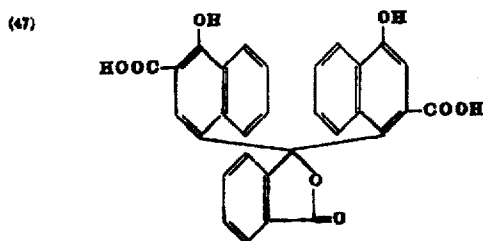
Page 7

Patent No. 3,647,437 Dated March 7, 1972

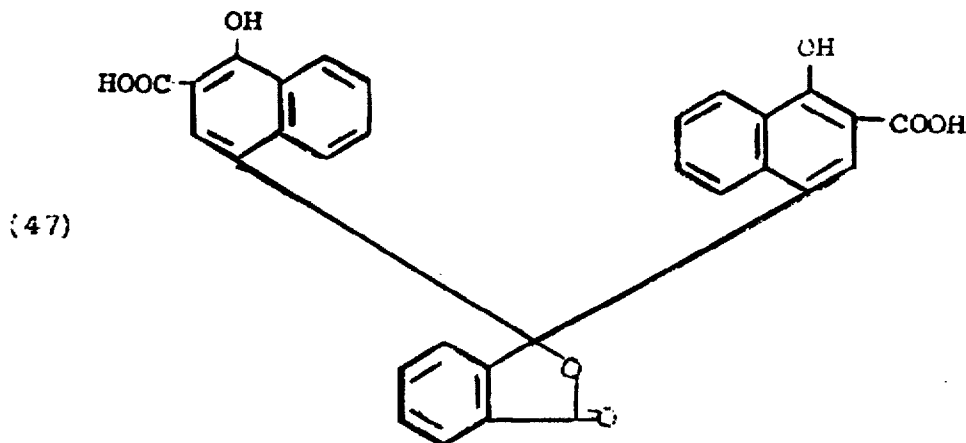
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 31, Formula (47)



should be



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CERTIFICATE OF CORRECTION

Page 8

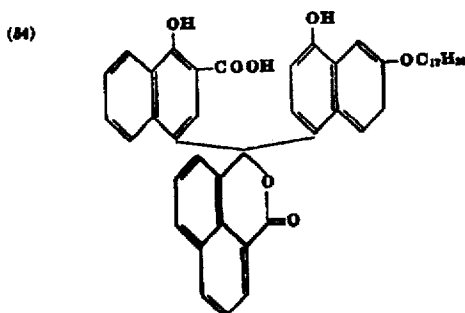
Patent No. 3,647,437

Dated March 7, 1972

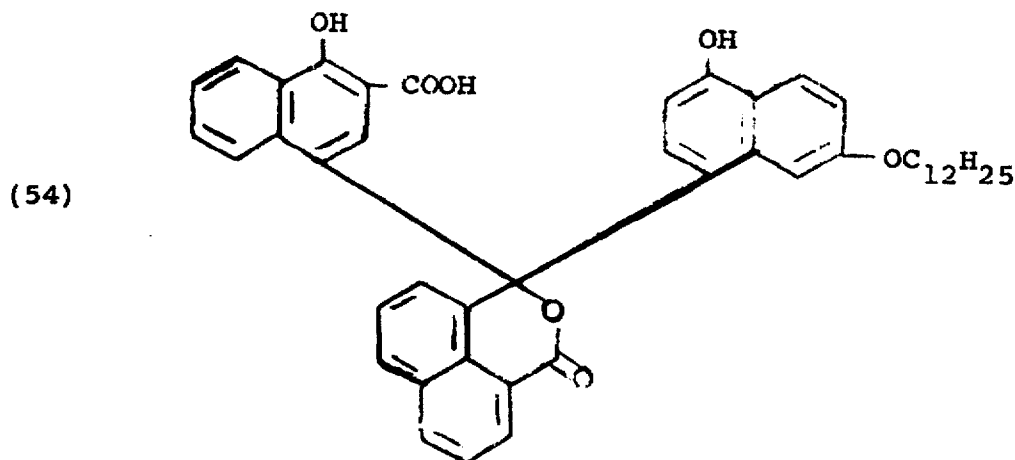
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 32, Formula (54)



should be



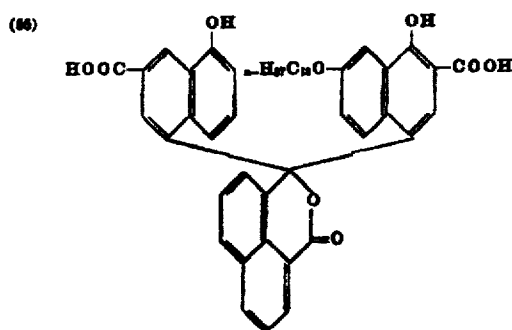
UNITED STATES PATENT OFFICE Page 9
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

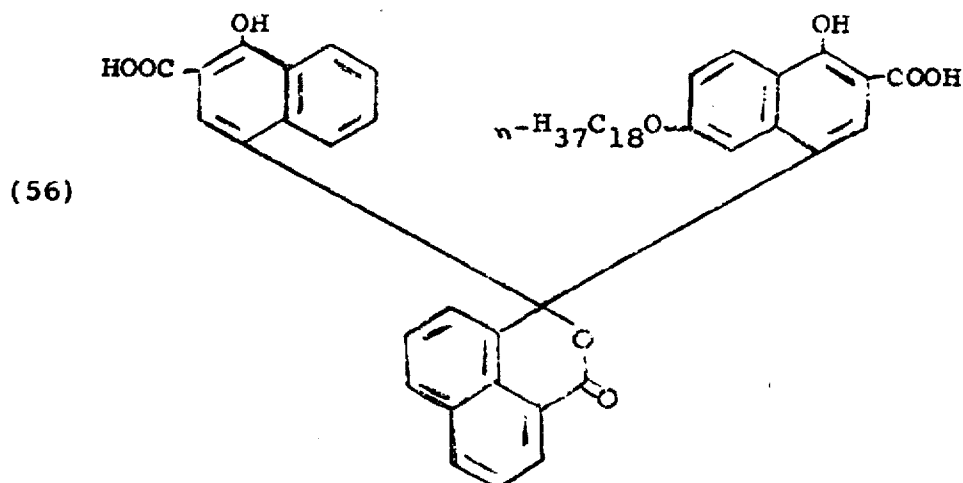
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 33, Formula (56)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

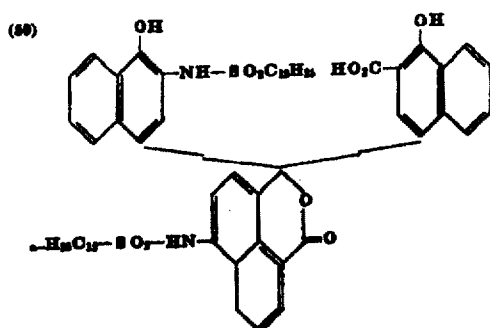
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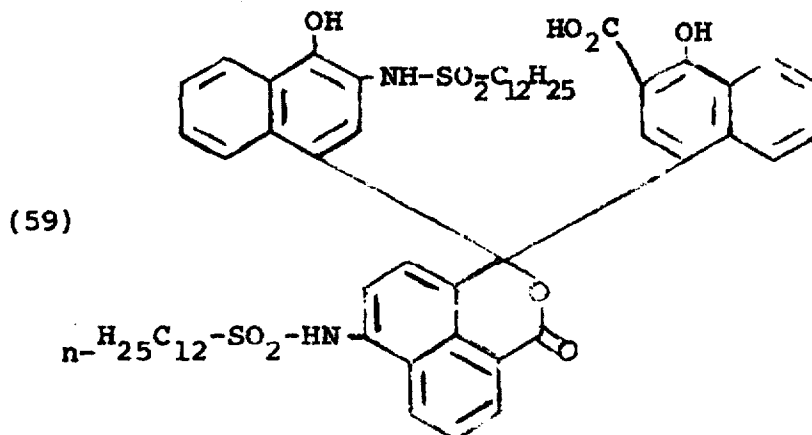
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 33, Formula (59)



should be



UNITED STATES PATENT OFFICE Page 11
CERTIFICATE OF CORRECTION

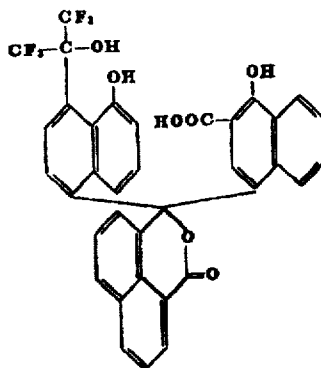
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

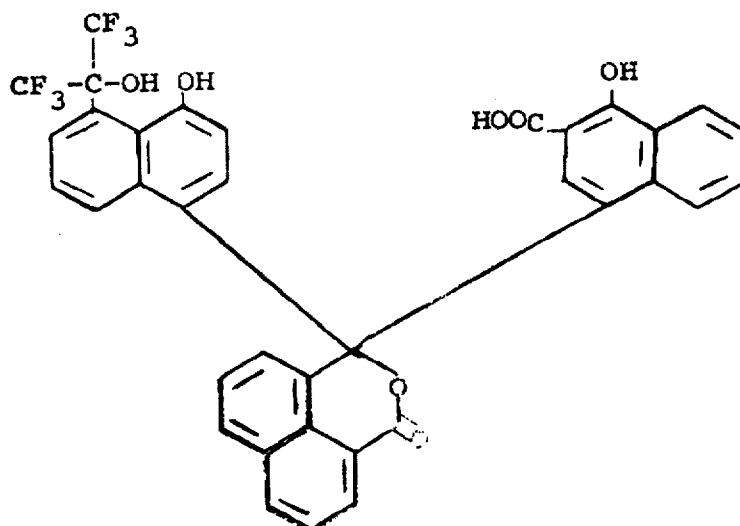
Column 34, Formula (65)

(66)



should be

(65)



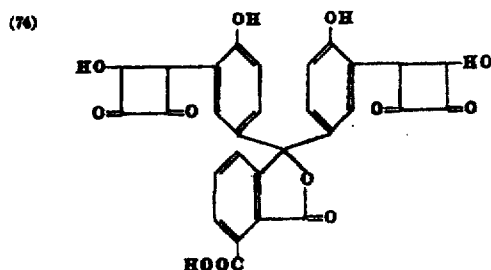
UNITED STATES PATENT OFFICE Page 12
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

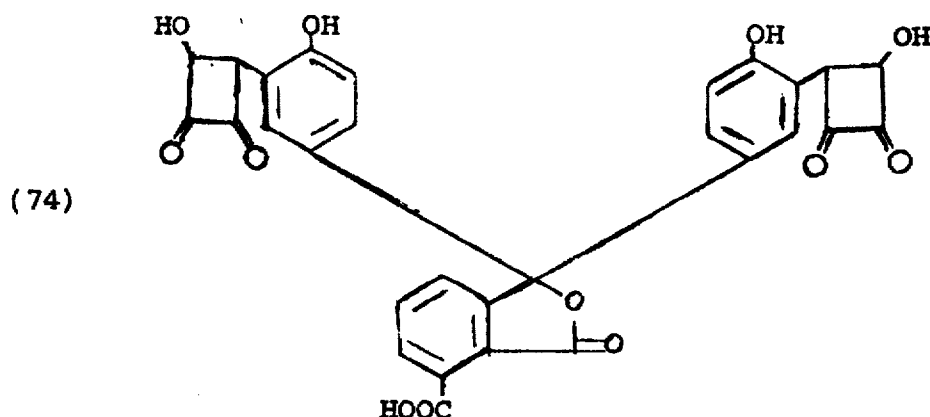
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 36, Formula (74)



should be



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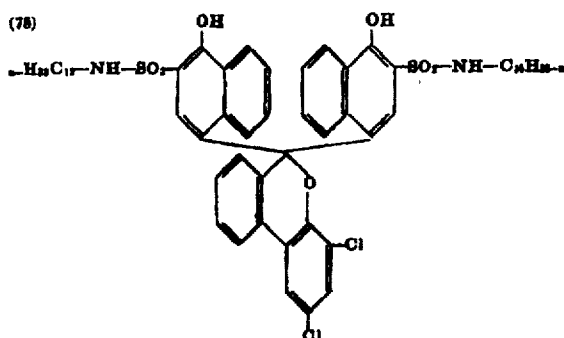
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

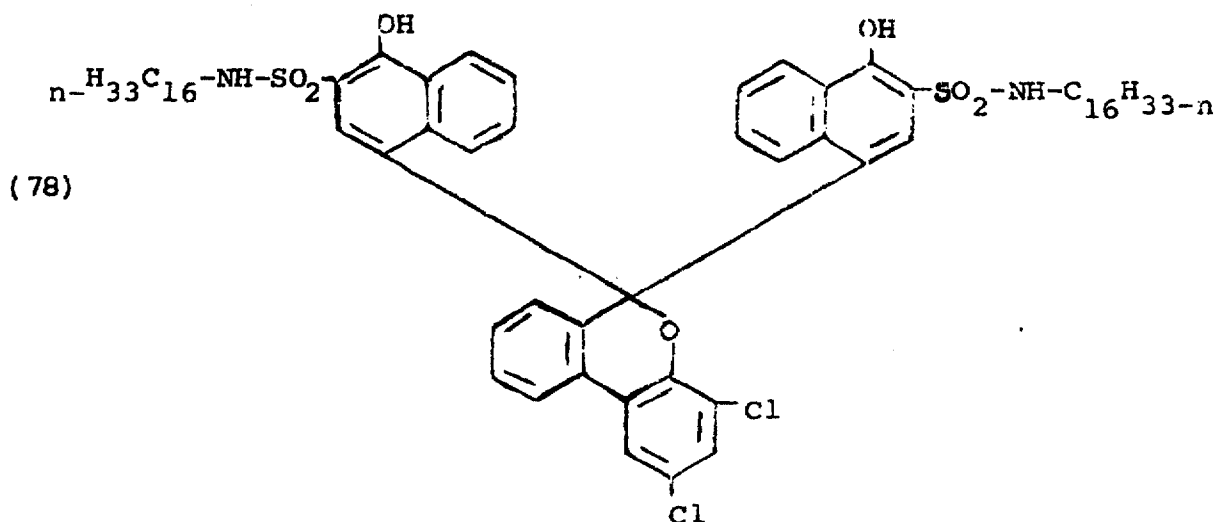
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 37, Formula (78)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

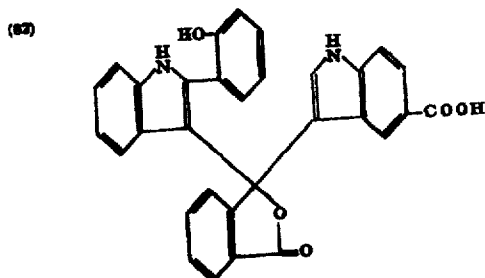
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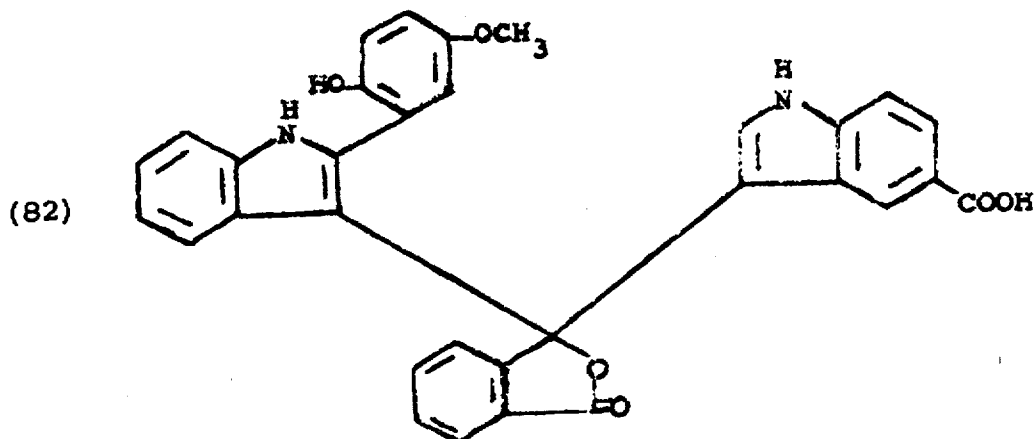
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 38, Formula (82)



should be



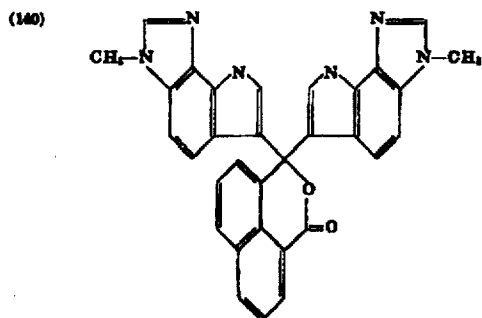
UNITED STATES PATENT OFFICE Page 15
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

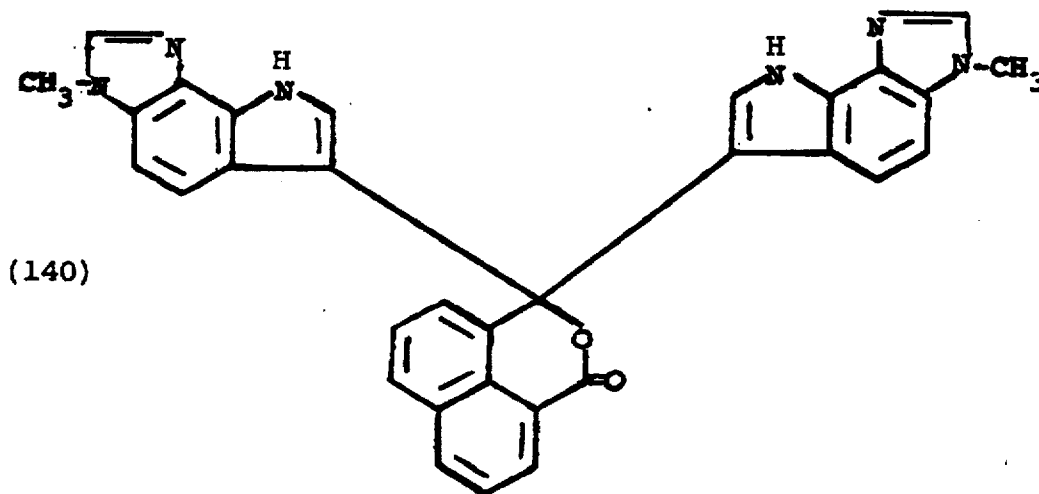
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 48, Formula (140)



should be



UNITED STATES PATENT OFFICE Page 16
CERTIFICATE OF CORRECTION

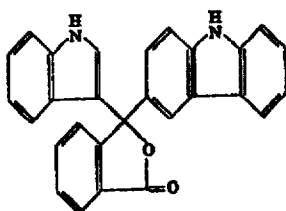
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

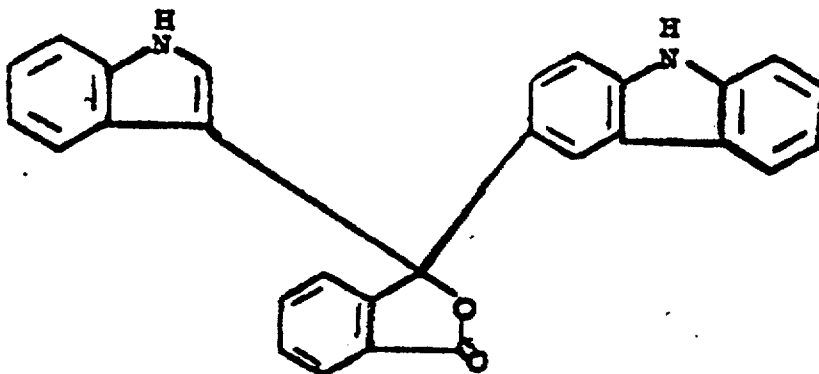
Column 48, Formula (142)

(142)



should be

(142)



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CERTIFICATE OF CORRECTION

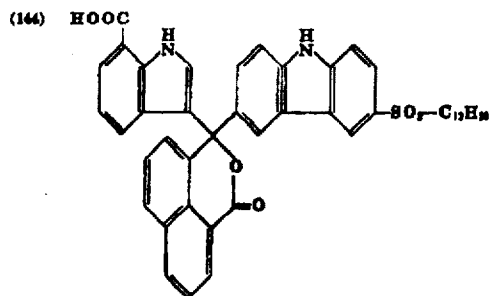
Patent No. 3,647,437

Dated March 7, 1972

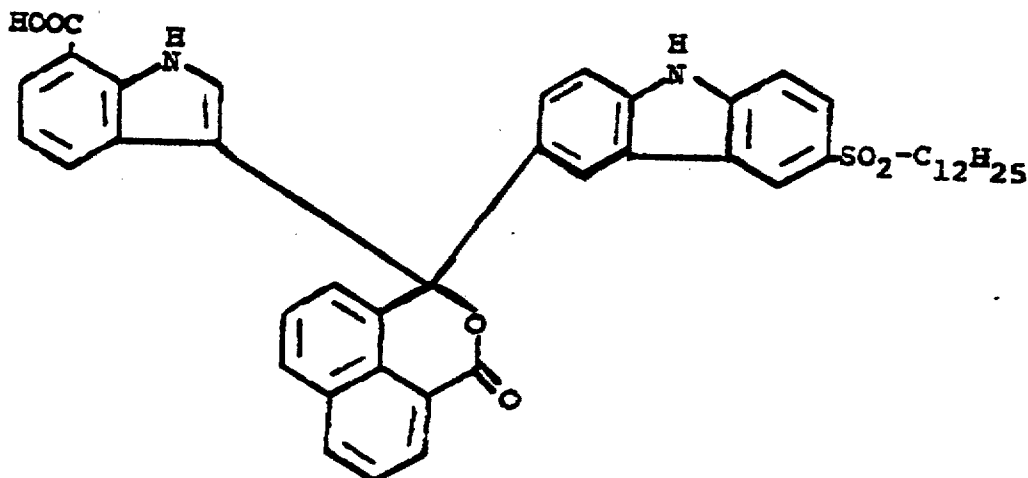
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 48, Formula (144)



should be



UNITED STATES PATENT OFFICE Page 18
CERTIFICATE OF CORRECTION

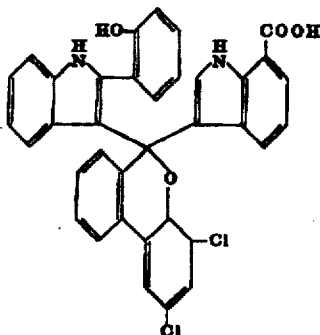
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

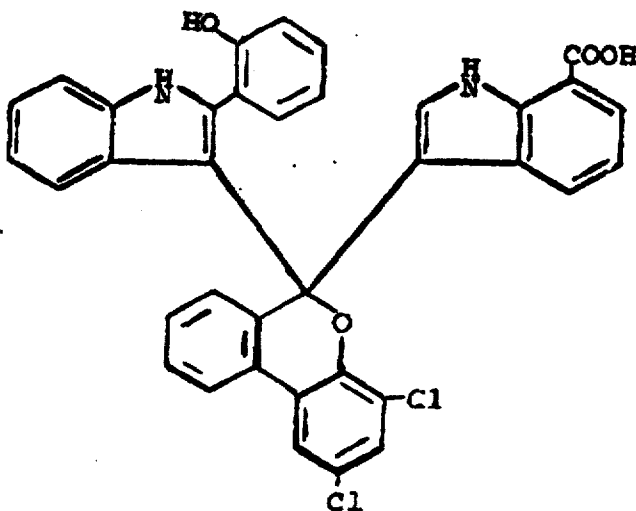
Column 49, Formula (148)

(148)



should be

(148)



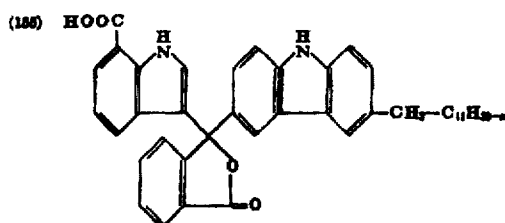
UNITED STATES PATENT OFFICE Page 19
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

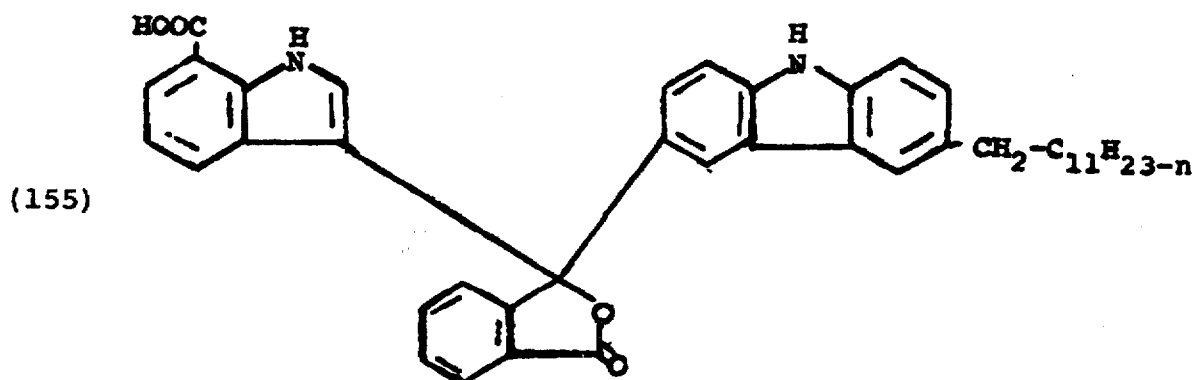
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 50, Formula (155)



should be



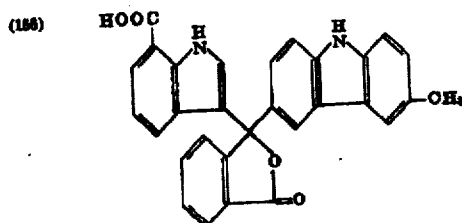
UNITED STATES PATENT OFFICE Page 20
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

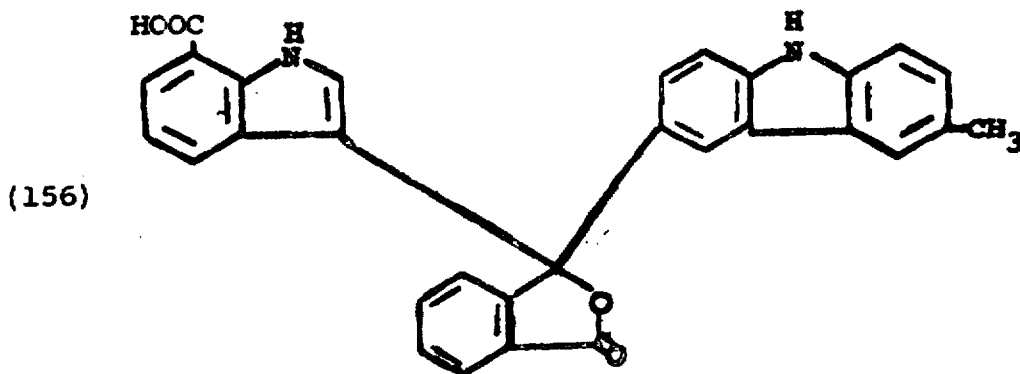
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 50, Formula (156)



should be



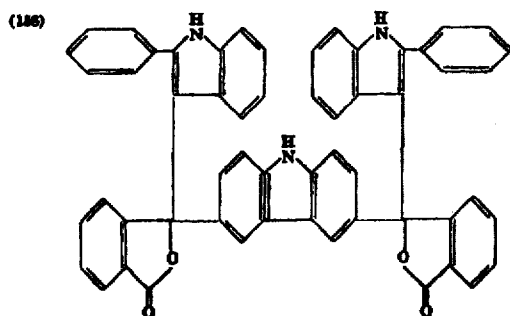
UNITED STATES PATENT OFFICE Page 21
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

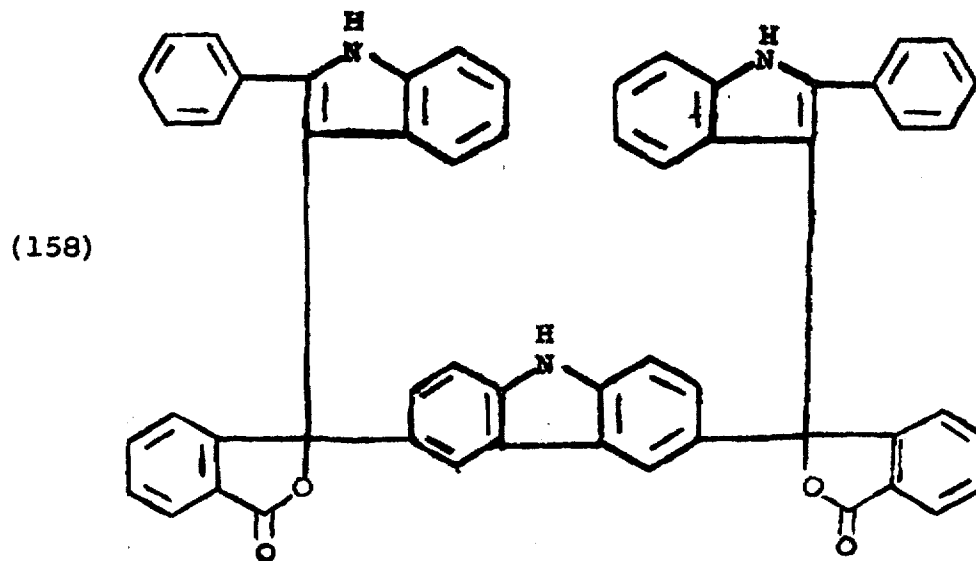
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 51, Formula (158)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

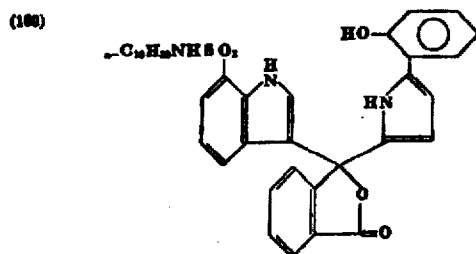
Page 22

Patent No. 3,647,437 Dated March 7, 1972

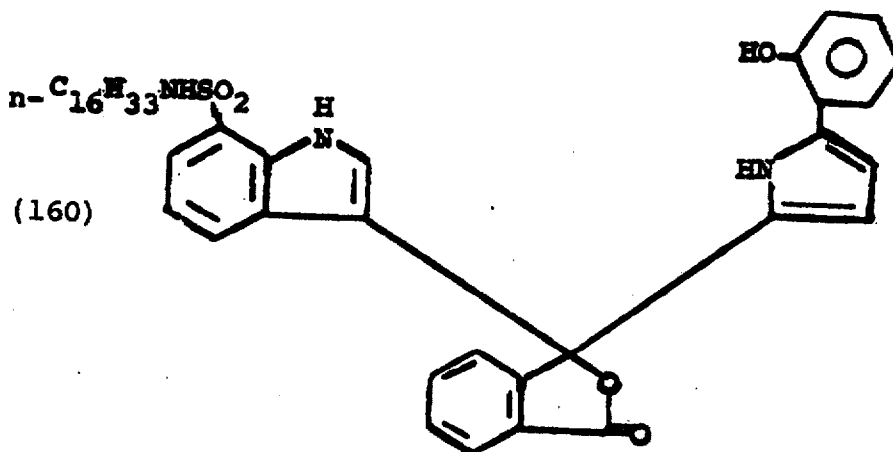
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 51, Formula (160)



should be



UNITED STATES PATENT OFFICE Page 23
CERTIFICATE OF CORRECTION

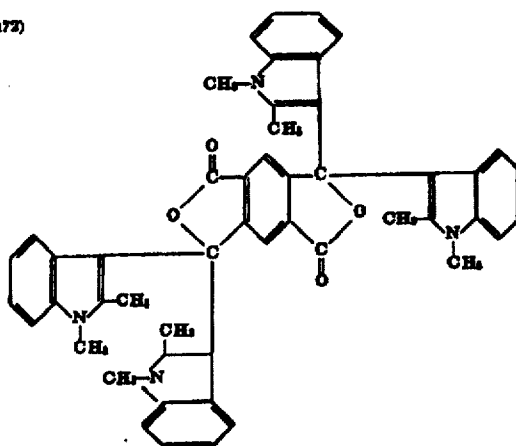
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 53, Formula (172)

(172)



should be

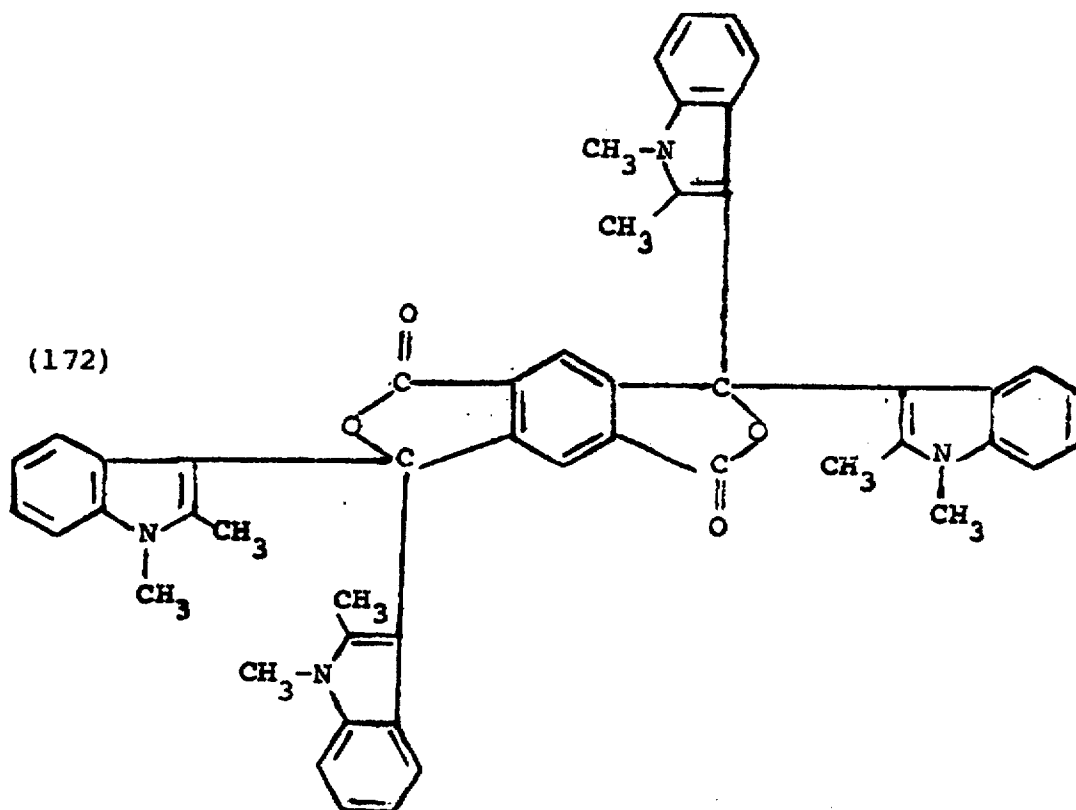
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 24

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:



Page 25

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

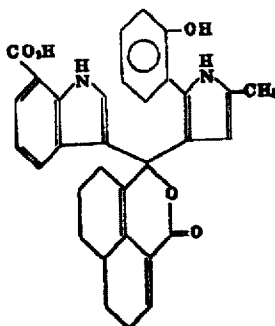
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

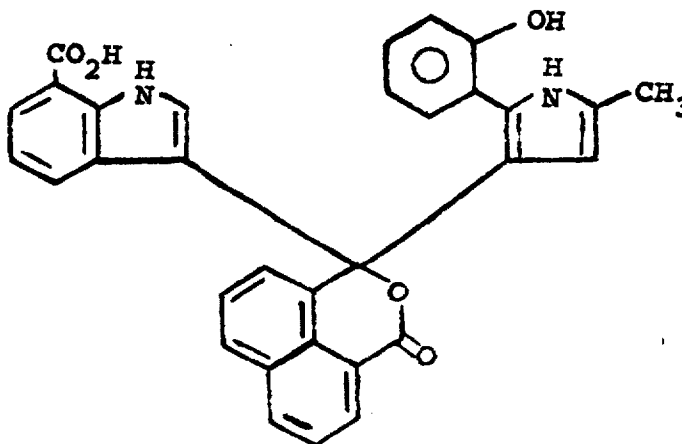
Column 54, Formula (175)

(176)



should be

(175)



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 26

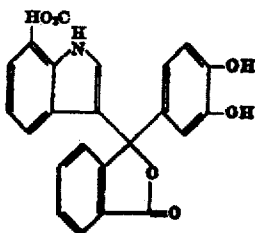
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

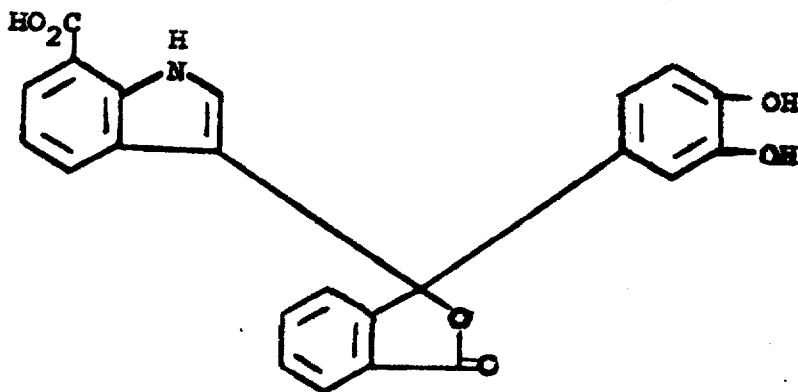
Column 57, Formula (192)

(192)



should be

(192)



UNITED STATES PATENT OFFICE Page 27
CERTIFICATE OF CORRECTION

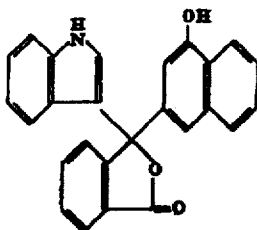
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

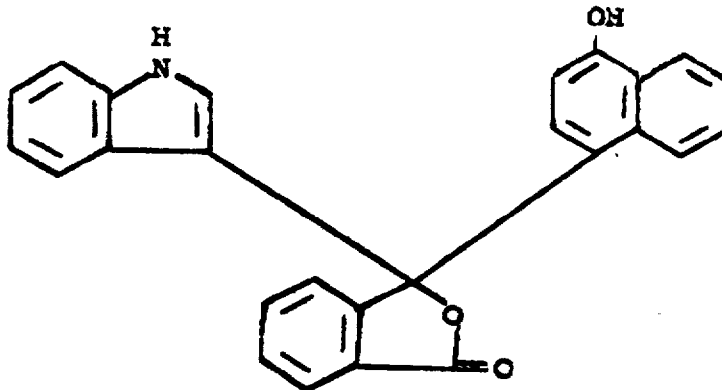
Column 57, Formula (196)

(106)



should be

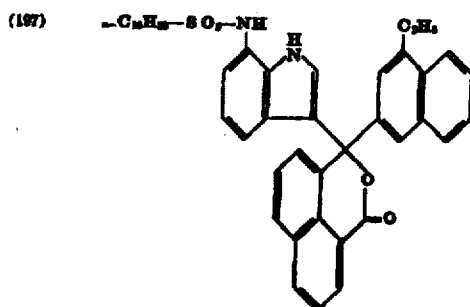
(196)



Page 28

Inventor(s) Edwin H. Land

Column 57, Formula (197)



(197)

Chemical structure (197) is a triaryl methane derivative. It features a central carbon atom bonded to three aromatic rings. The top-left ring is an indole-3-yl group, substituted with an $n\text{-C}_{16}\text{H}_{33}\text{-SO}_2\text{-}$ group at the 2-position. The top-right ring is a 2-ethylphenyl group, substituted with a C_2H_5 group at the 2-position. The bottom ring is a fluorenone-9-yl group, where the central carbon is bonded to the 9-position of a fluorenone system.

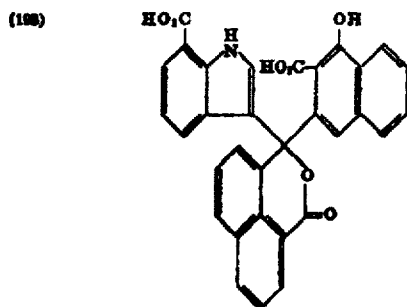
UNITED STATES PATENT OFFICE Page 29
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

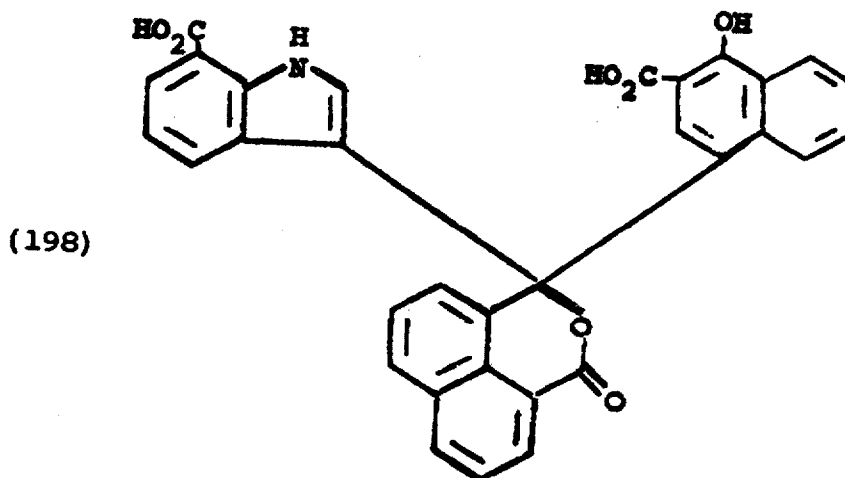
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (198)



should be



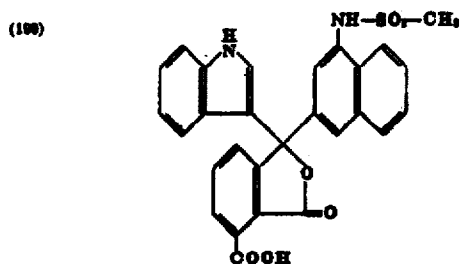
UNITED STATES PATENT OFFICE Page 30
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

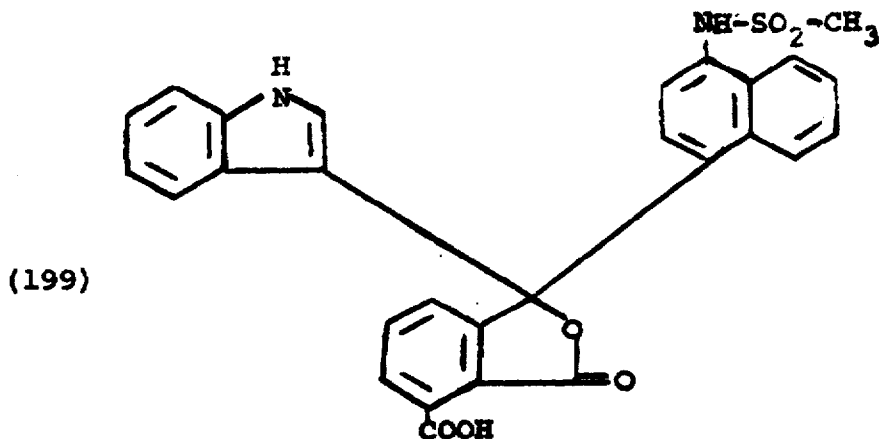
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (199)



should be



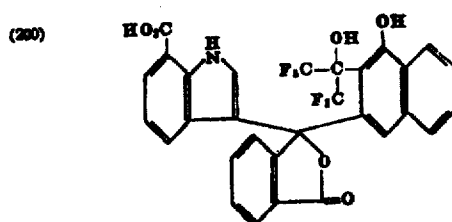
UNITED STATES PATENT OFFICE Page 31
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

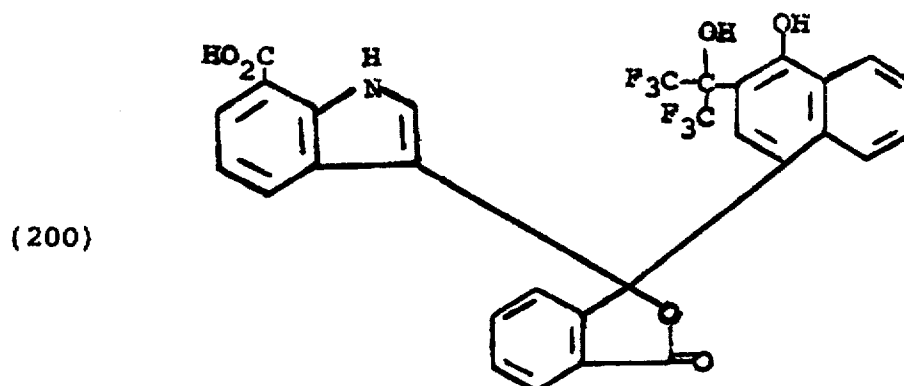
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (200)



should be



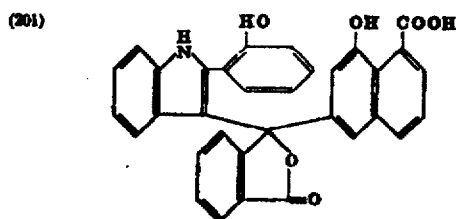
UNITED STATES PATENT OFFICE Page 32
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

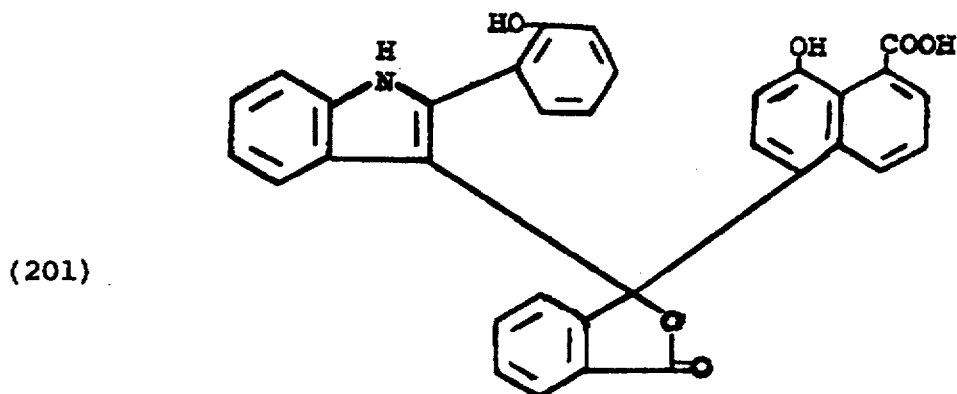
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (201)



should be



44

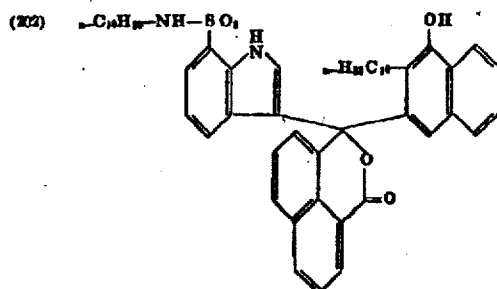
UNITED STATES PATENT OFFICE Page 33
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

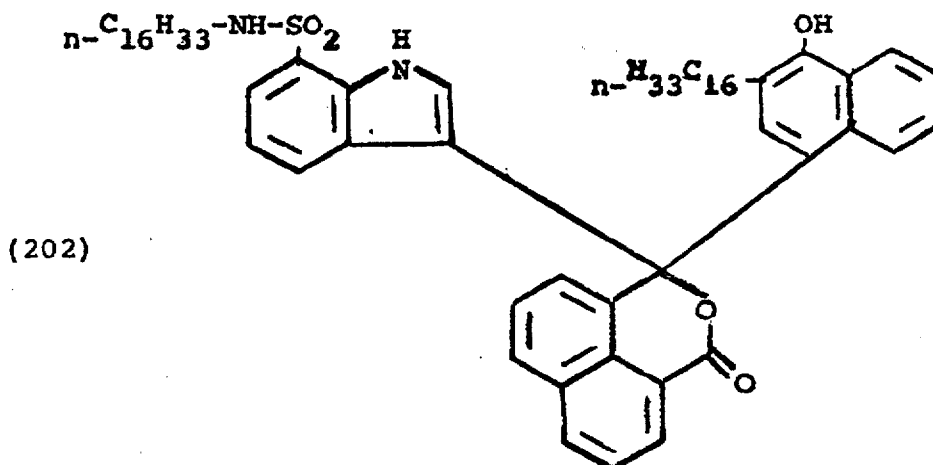
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (202)



should be



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

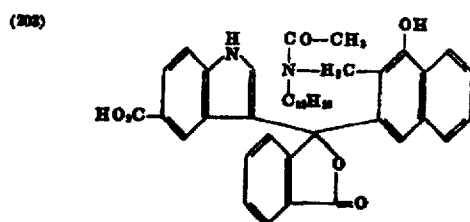
Page 34

Patent No. 3,647,437 Dated March 7, 1972

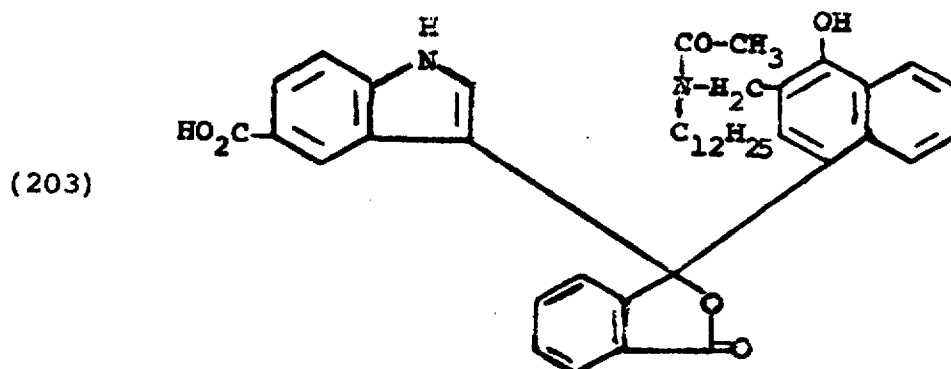
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 58, Formula (203)



should be



446

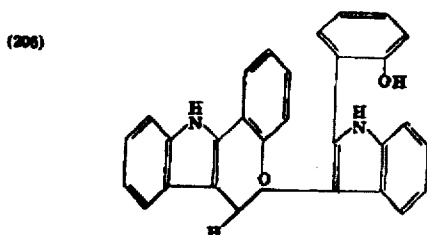
UNITED STATES PATENT OFFICE Page 35
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

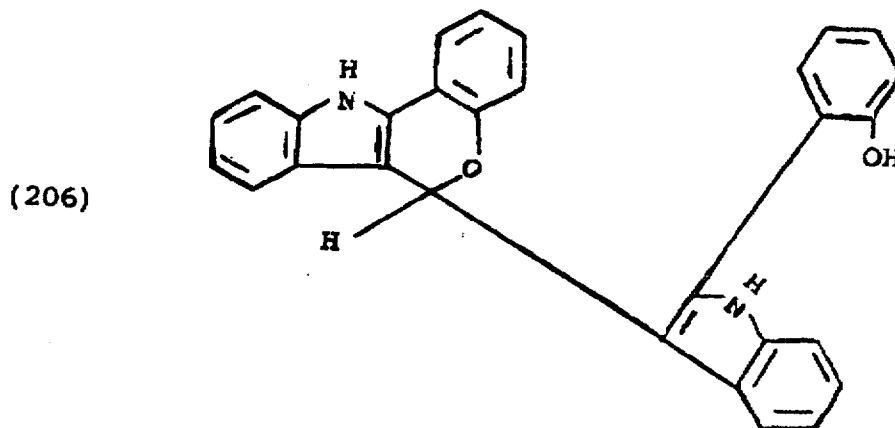
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 59, Formula (206)



should be



Page 36

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

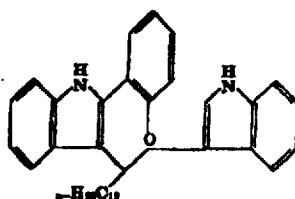
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

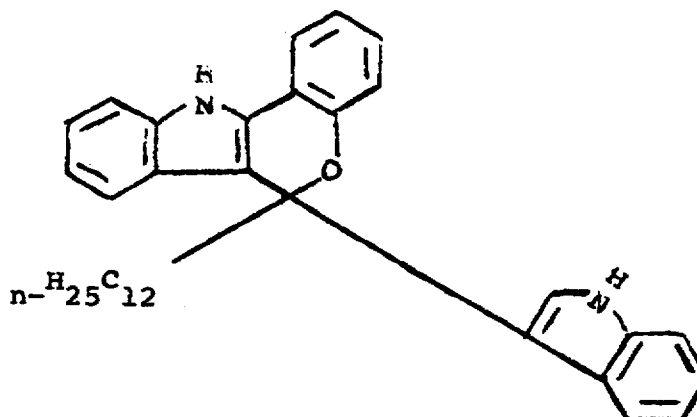
Column 59, Formula (207)

(207)



should be

(207)



Column 60, lines 64 and 65, after "preferably"
delete " ~ 0.2 micron in diameter and preferably".

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CERTIFICATE OF CORRECTION

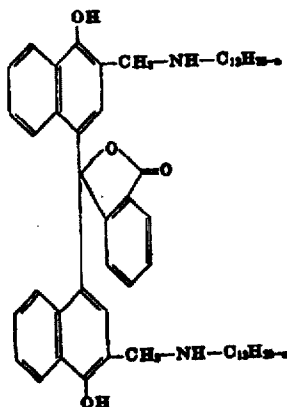
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) _____

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

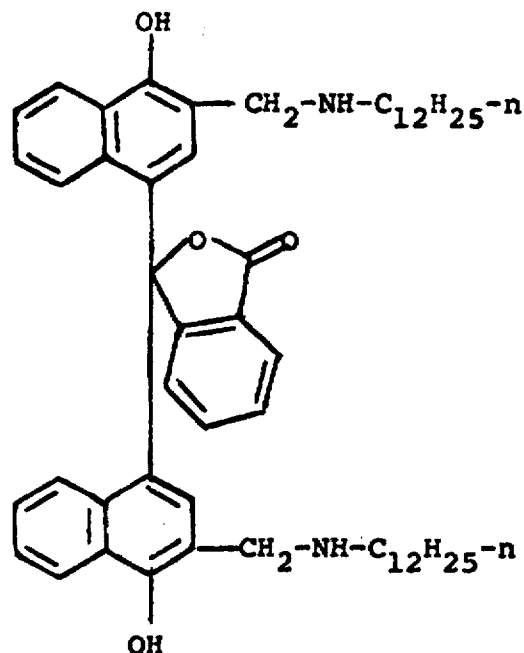
Column 62, Formula (210)

(210)



should be

(210)



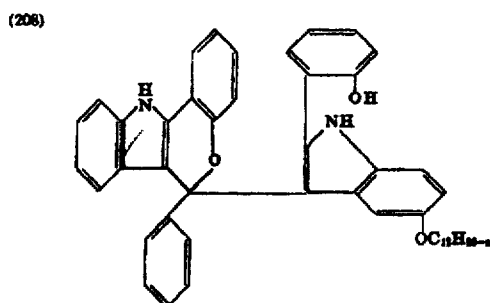
UNITED STATES PATENT OFFICE Page 38
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

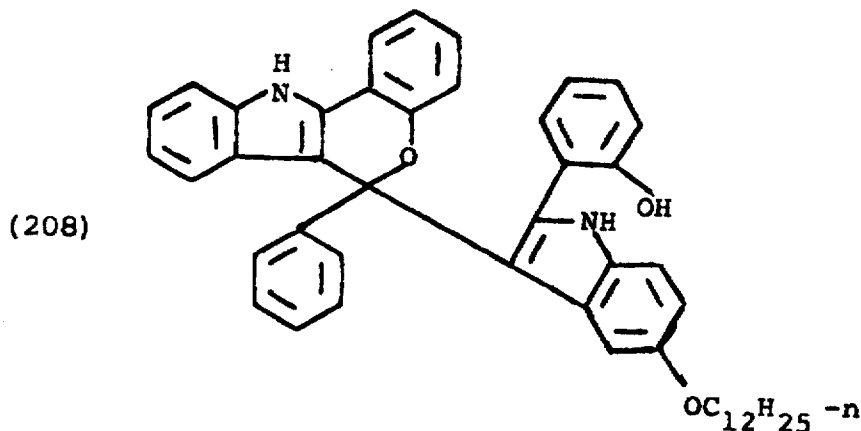
Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 62, Formula (208)



should be



UNITED STATES PATENT OFFICE Page 39
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 75, line 65, "precedure" should be --procedure--.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 40

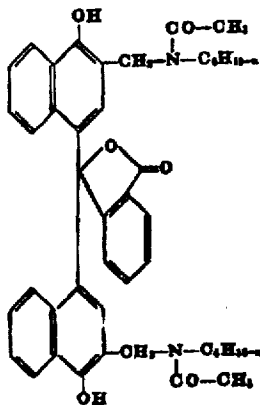
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

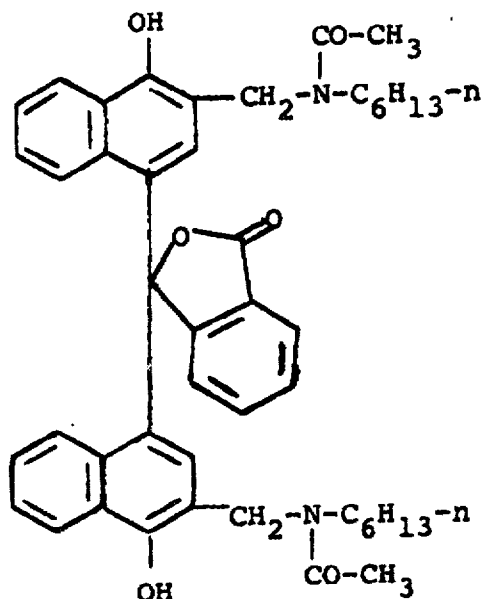
Column 63, Formula (216)

(216)



should be

(216)



UNITED STATES PATENT OFFICE Page 41
CERTIFICATE OF CORRECTION

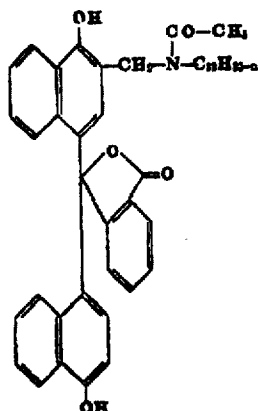
Patent No. 3,647,437

Dated March 7, 1972

Inventor(s) Edwin H. Land

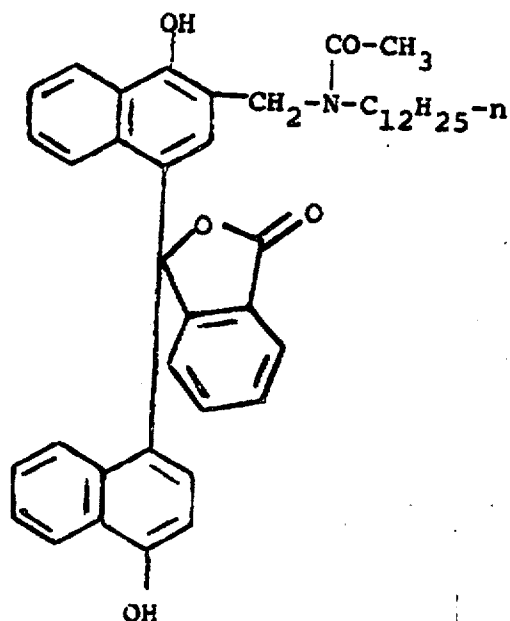
It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:
Column 64, Formula (218)

(218)



should be

(218)



UNITED STATES PATENT OFFICE Page 42
CERTIFICATE OF CORRECTION

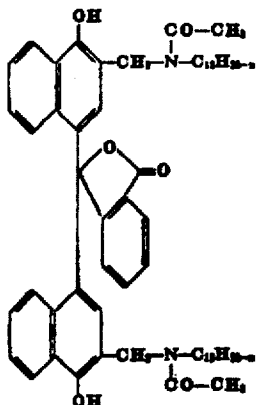
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

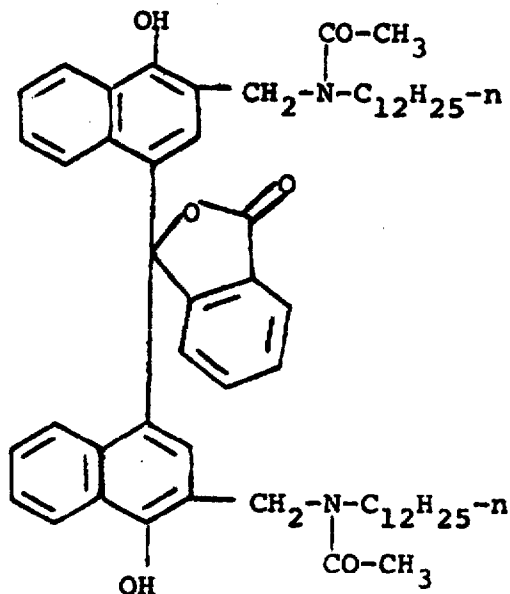
Column 64, Formula (221)

(221)



should be

(221)



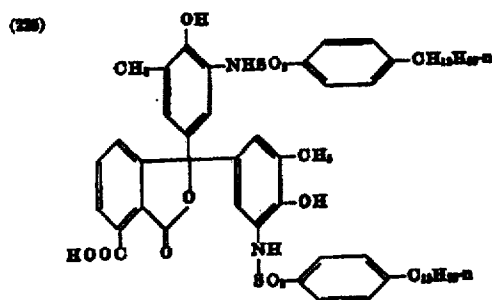
UNITED STATES PATENT OFFICE Page 43
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 65, Formula (225)



should be

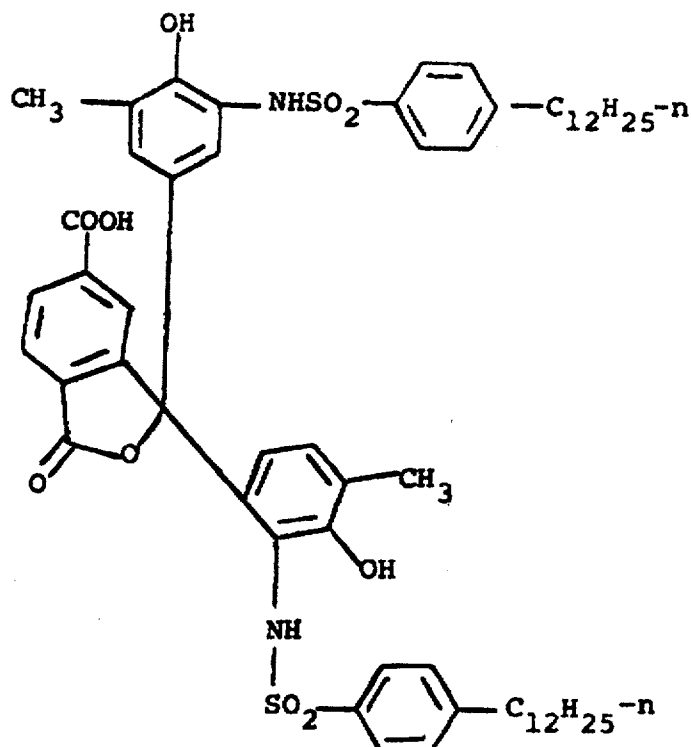
UNITED STATES PATENT OFFICE Page 44
CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

(225)



UNITED STATES PATENT OFFICE Page 45
CERTIFICATE OF CORRECTION

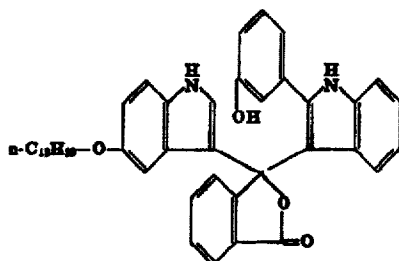
Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

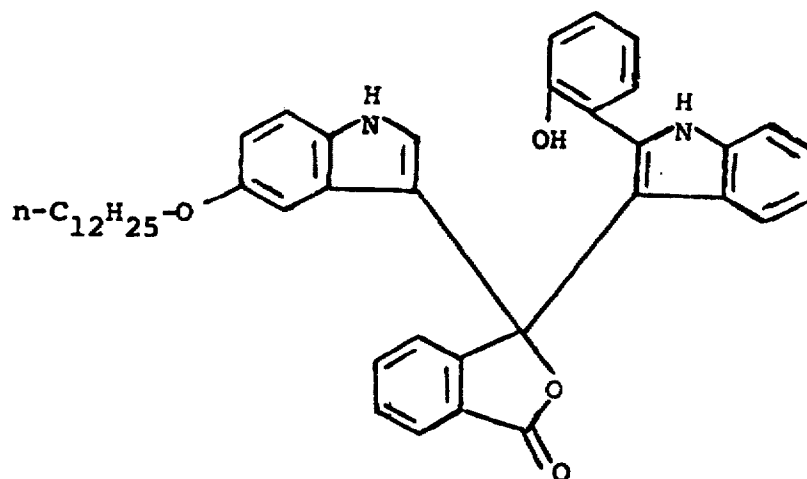
Column 67, Formula (A)

(A)



should be

(A)



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CERTIFICATE OF CORRECTION

Patent No. 3,647,437

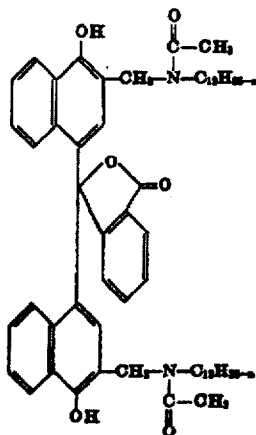
Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

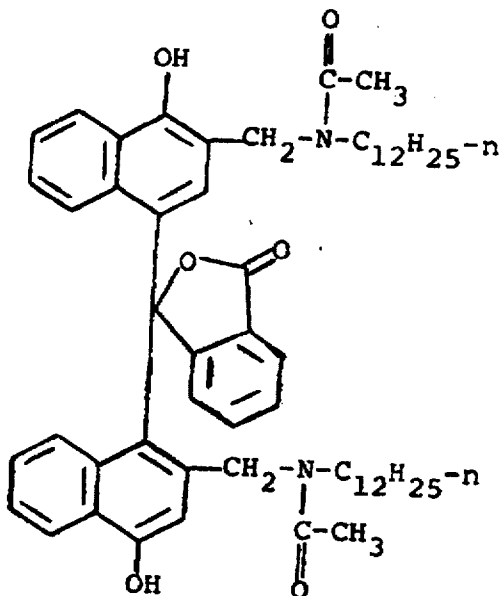
Column 67, Formula (C)

(D)



should be

(C)



UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Page 47

Patent No. 3,647,437

Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 67, line 71, "compsoition's" should be --compositions--.

Column 69, line 73, "101,842" should be --101,841--.

Column 70, line 55, "agent(s)" should be --agent(s)'--.

Column 75, line 59, "be" should be --been--.

Column 79, claim 33, lines 51 and 52, after "material" delete "is exposed imagewise and said exposed photosensitive material".

Column 80, claim 39, line 27, "claimed" should be --defined--.

Column 80, claim 39, line 29, after "including" insert --said--.

Column 80, claim 41, line 34, delete "diffusion transfer" and insert --dye--.

Column 81, claim 58, line 62, after "pigment" insert --comprises--.

Column 82, claim 62, line 1, "composition" should be --composite--.

Column 82, claim 62, line 4, "emulsions" should be --emulsion--.

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CERTIFICATE OF CORRECTION

Patent No. 3,647,437 Dated March 7, 1972

Inventor(s) Edwin H. Land

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 84, claim 76, line 54, "comprising" should be --comprises--.

Column 86, claim 83, line 45, after "each insert --of--.

Column 86, claim 83, line 46, after "being" insert --silver halide developing agents and being--.

Column 87, claim 86, line 63, "to" should be --of--.

Signed and sealed this 2nd day of April 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents