

**PHOTOGRAPHIC PROCESSES AND PRODUCTS  
EMPLOYING AMINOMETHYL-SUBSTITUTED  
PHENOLIC PHTHALEINS AS OPTICAL FILTER  
AGENTS**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

The present invention relates to novel chemical compounds, and more specifically, it relates to a new class of phthalein indicator dyes. In a particular aspect it relates to certain phthaleins useful as optical filter agents in photographic processes for protecting an exposed photosensitive material from post-exposure fogging during development in the presence of extraneous incident light and to such photographic uses.

**2. Description of the Prior Art**

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 sheet-like elements, the desired image being carried by one of said sheet-like 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 image-wise 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.

U. S. Pat. No. 3,415,644 discloses a composite photosensitive structure, particularly adapted for use in reflection type photographic diffusion transfer color processes. This structure comprises a plurality of essential layers including, in sequence, a dimensionally stable opaque layer; one or more silver halide emulsion layers having associated therewith dye image-providing material which is soluble and diffusible, in alkali, at a first pH, as a function of the point-to-point degree of its associated silver halide emulsion's exposure to incident actinic radiation; a polymeric layer adapted to receive solubilized dye image-providing material diffusing thereto; a polymeric layer containing sufficient acidifying capacity to effect reduction of a processing composition from the first pH to a second pH at which the dye image-providing material is substantially nondiffusible; and a dimensionally stable transparent layer. This structure may be exposed to incident actinic radiation and processed by interposing, intermediate the silver halide emulsion layer and the reception layer, an alkaline processing composition providing the first pH and containing a light-reflecting agent, for example, titanium dioxide to provide a white background. The light reflecting agent (referred to in said patent as an "opacifying agent") also performs an opacifying function, i.e., it is effective to mask the developed silver halide emulsions and also acts to protect the photoexposed emulsions from postexposure fogging by light passing through the transparent layer if the photoexposed film unit is removed from the camera before image formation is complete.

In a preferred embodiment, the composite photosensitive structure includes a rupturable container, retain-

ing the alkaline processing composition having the first pH and light-reflecting agent, fixedly positioned extending transverse a leading edge of the composite structure in order to effect, upon application of compressive pressure to the container, discharge of the processing composition intermediate the opposed surfaces of the reception layer and the next adjacent silver halide emulsion.

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

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

In the copending U. S. Pat. application Ser. No. 786,352 of Edwin H. Land, filed Dec. 23, 1968, now abandoned, and Ser. No. 101,968 filed Dec. 28, 1970, now U.S. Patent No. 3,647,437, in part a continuation of Ser. No. 786,352, an organic light-absorbing reagent (or optical filter agent), such as a dye, which is present as a light-absorbing species at the first pH and which may be converted to a substantially non-light-absorbing species at the second pH is used in conjunction with the light-reflecting agent to protect the selectively exposed silver halide emulsions from post-exposure fogging when development of the photoexposed emulsions is conducted in the presence of extraneous incident actinic radiation impinging on the transparent layer of the film unit.

In the processes of aforementioned applications Ser. Nos. 786,352 and 101,968, and in other photographic processes, it is preferred to use, as the optical filter agent, a dye that is substantially non-diffusible in the photographic processing composition in order to achieve optimum efficiency as a radiation filter and to prevent diffusion of optical filter agent into layers of the film unit where its presence may be undesirable. The present invention is concerned with pH-sensitive dyes, namely, certain phthaleins of hydroxy-substituted carbocyclic aryl compounds, i.e., phenols and 1-

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and alkaryl groups, such as, phenyldecyl, phenyloctyl, phenylhexyl, p-octylphenyl and p-dodecylphenyl. Examples of acyl substituents are those of the formula



wherein R''' is alkyl, aryl, or alkaryl, such as, the respective groups enumerated above.

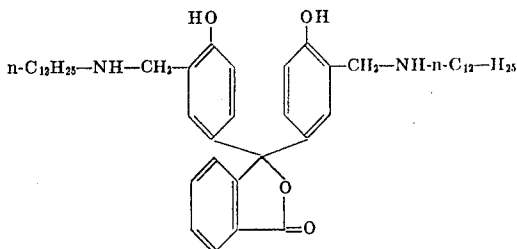
Since the  $-\text{CH}_2-\text{NRR}'$  group or groups should render a given dye substantially non-diffusible in a given aqueous solution, the respective R' substituent(s) will be selected so that together with the respective R substituent(s), the resulting dye is substantially immobile in solution. For example, when the R substituent(s) is hydrogen, relatively long chain alkyl groups, such as, dodecyl or octadecyl may be selected as the R' substituent(s), whereas an alkyl group with a lesser number of carbon atoms may be adequate to achieve substantial non-diffusibility of the dye where the R substituent(s) is a relatively long chain group(s).

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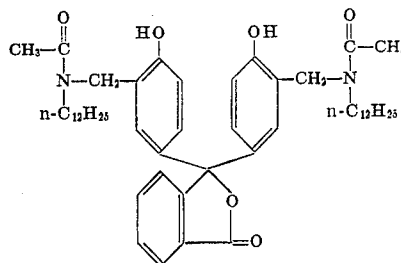
The indicator dyes defined above and as represented in the foregoing formula may contain substituents other than those specified on the p-hydroxycarbocyclic aryl radicals and/or the ring-closing moiety. Typical substituents include alkyl, such as, methyl, ethyl, propyl; alkoxy, such as, methoxy, ethoxy, butoxy; halo, such as, fluoro, chloro, bromo; and solubilizing groups as exemplified by hydroxy, carboxy and sulfo. It will be recognized, however, that such additional substituents should not interfere with the function of the dye for its intended ultimate use and also that substituents, such as, the solubilizing or other groups may be included in the  $-\text{CH}_2-\text{NRR}'$  group(s) rather than being substituted directly on the carbocyclic radicals and/or the ring-closing moiety. Preferably, the dyes of the present invention are symmetrical, i.e., bis phthalides and naphthalides wherein the two phenyl or the two naphthyl radicals contain the same substituents in the same positions so that they are identical.

Specific examples of indicator dyes within the scope of the present invention are as follows:

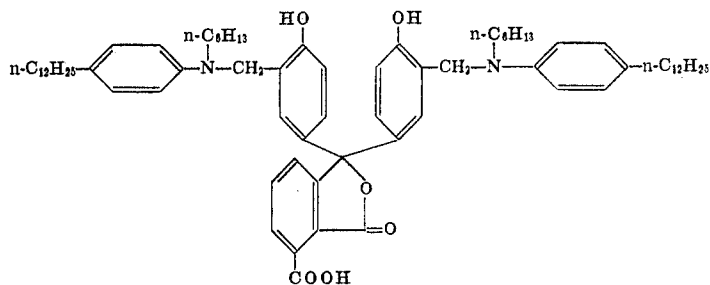
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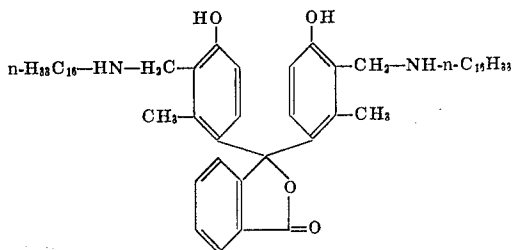
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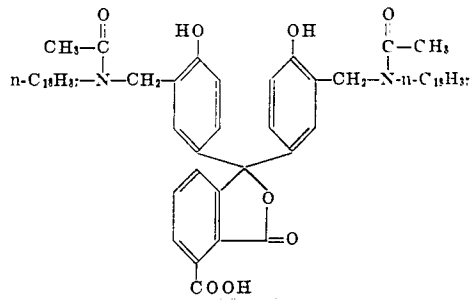
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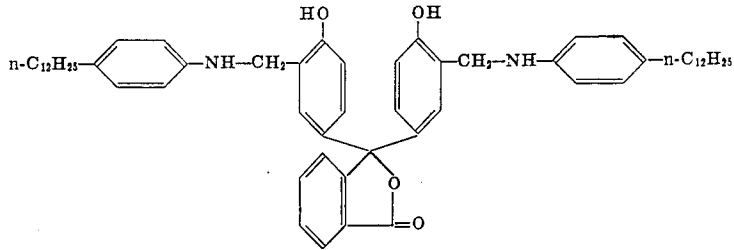
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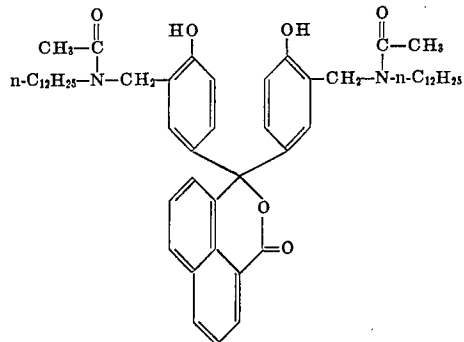
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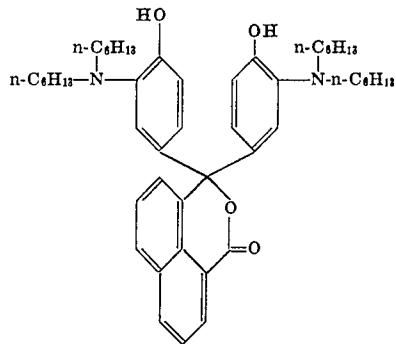
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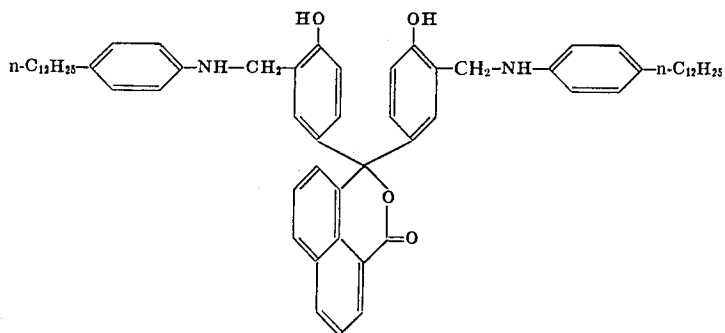
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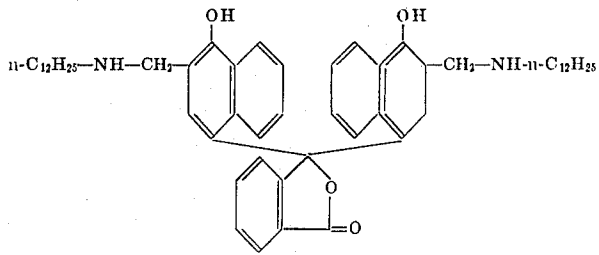
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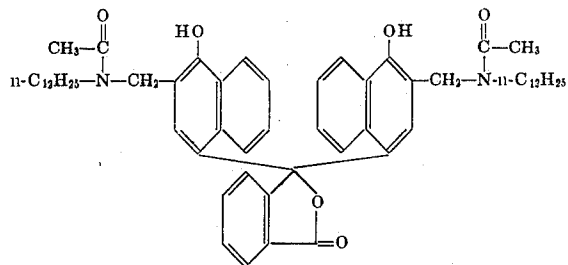
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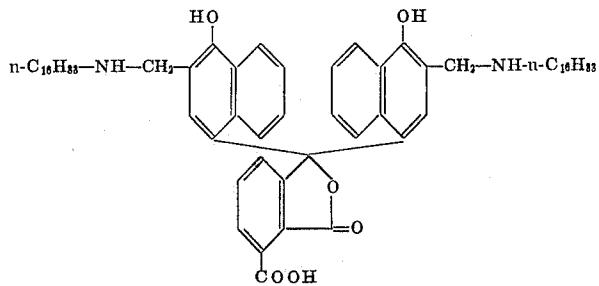
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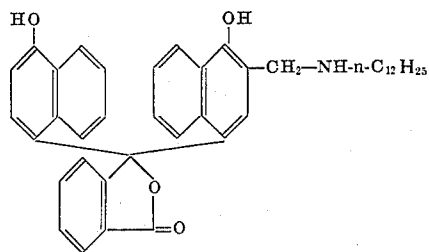
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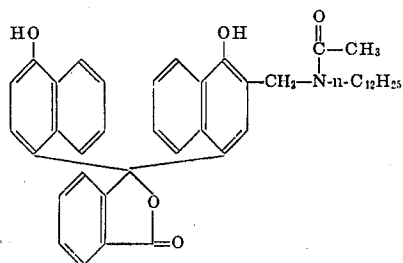
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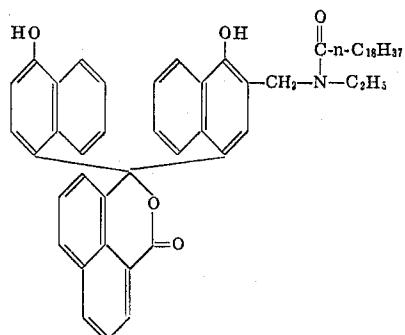
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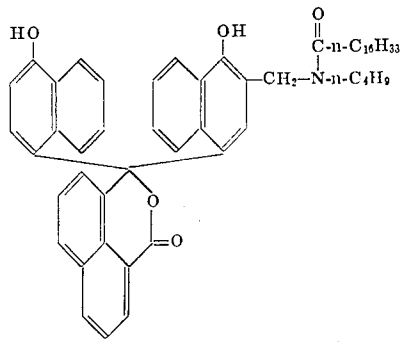
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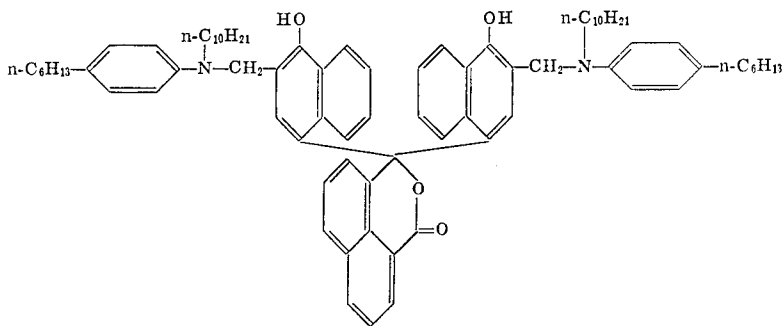
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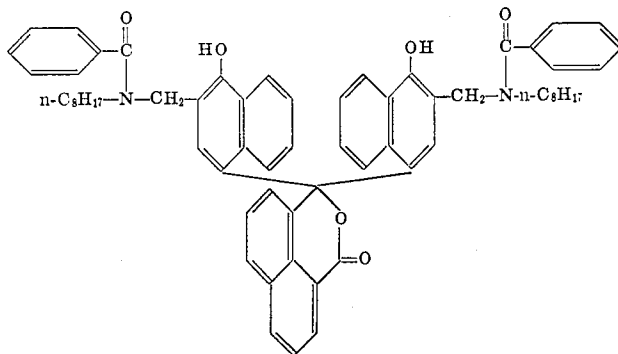
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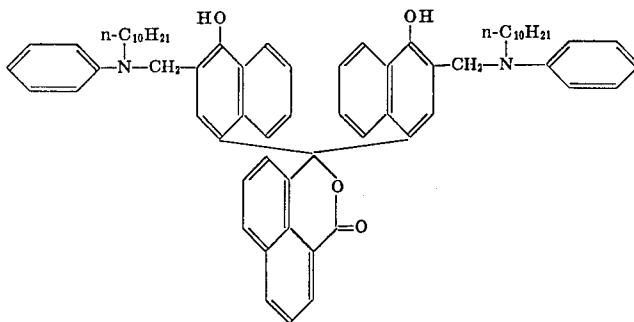
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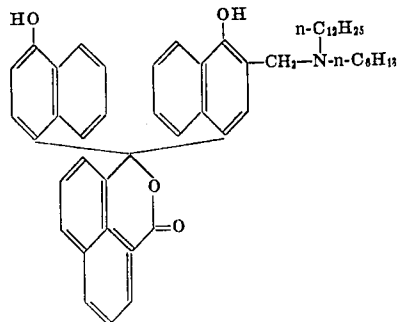
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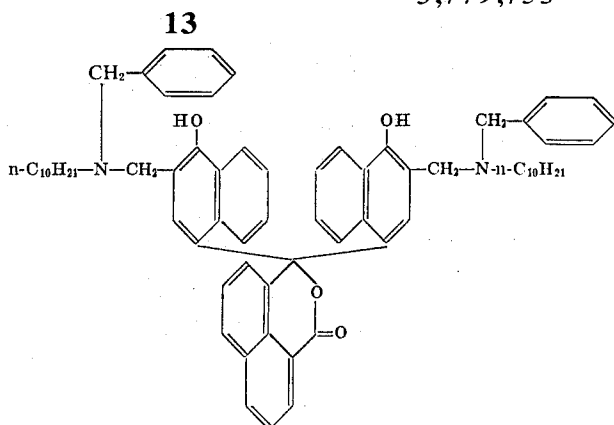
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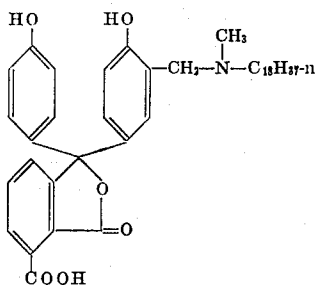
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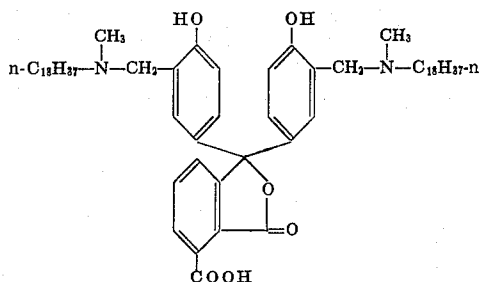
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In preparing the dyes of the present invention, the  $-\text{CH}_2\text{-NRR}'$  group or groups may be introduced by reacting a dye intermediate and/or a phthalide or naphthalide indicator dye with formaldehyde and a primary or secondary amine. For example, a dye intermediate, such as, 3-hydroxy-3-(4'-hydroxynaphthyl) naphthalide-1,8 may be condensed with formaldehyde and the appropriate amine to yield the corresponding (3'- $\text{CH}_2\text{-NRR}'$ -4'-hydroxynaphthyl) naphthalide intermediate. This intermediate may then be reacted with a 1-naphthol under Friedel Crafts conditions to yield the complete dye. The naphthol reacted with the dye intermediate may contain a  $-\text{CH}_2\text{-NRR}'$  group or this group may be introduced subsequent to forming the complete dye by reacting the complete dye with formaldehyde and amine. Where the R substituent of the methylamino group(s) is hydrogen, the dye intermediate or the complete dye may be reacted with an acylating agent, e.g., acetyl chloride to convert the amino to amido group(s). By employing the foregoing procedure, phenol and 1-naphthol phthalides and naphthalides may be prepared which contain one or two  $-\text{CH}_2\text{-NRR}'$  groups, the same or different.

As noted above, the indicator dyes of the present invention are preferably symmetrical. Both phenol and both naphthol radicals contain the same substituents in the same positions including identical  $-\text{CH}_2\text{-NRR}'$  groups. Such dyes may be prepared more conveniently by simply reacting a phenol or 1-naphthol phthalide or

naphthalide with formaldehyde and an amine and then treating product with an acylating agent where appropriate and desired to produce the amido group.

It will be appreciated that the phenol or 1-naphthol radical(s) of the phthalide dye or dye intermediate employed as the starting material should have a free 2-position, i.e., a free position ortho to the p-hydroxy group for the condensation reaction with formaldehyde and the amine. The amine used may be any primary amine that will provide the desired R' substituent described above or any secondary amine that will provide the desired R and R' substituents. Where the methylamino groups are subsequently acylated, any of the agents commonly used in acylation reactions may be employed. Both the condensation reaction and acylation reaction may be carried out in a conventional manner.

The following Examples are given to further illustrate the present invention and are not intended to limit the scope thereof.

#### EXAMPLE 1

Preparation of the compound of formula (10).

Analytical grade 1-naphtholphthalide-2 $\text{CHCl}_3$  (2 equivalents) was dissolved in ethanol (1g./5ml.) in a 3-neck round-bottom flask fitted with mechanical stirrer, thermometer, and dropping funnel. n-Dodecyl amine (5 equivalents) was dissolved in ethanol

(1g./10ml.) and added in one portion to the reaction vessel. To this well-stirred solution, formalin (containing 2.1 equivalents formaldehyde) in ethanol (1 ml./5ml.) was added dropwise over 1 hour at a rate such that the temperature of the reaction mixture did not exceed 30°C. and the mixture stirred at room temperature about 14 hours. The reaction mixture was filtered and washed with ethanol into a round-bottom flask and evaporated on a rotary evaporator with the heating bath maintained at < 30°C. The residual dark paste was triturated with excess hexane (approximately 1 g./40ml.) until an easily filterable solid was obtained. The solid was collected and triturated again with hexane, collected and washed well with hexane to ensure that all unconverted dodecylamine had been removed. An analytical sample was obtained by crystallization from boiling hexane. The bulk of the crude sample was dissolved in hot chloroform (1g./5ml.), filtered, and diluted with 10 volumes hexane and allowed to stand several hours. The title compound was recovered in about 70-80 percent by weight.

#### EXAMPLE 2

Preparation of the compound of formula (11):

The product obtained in Example 1 above was dissolved in dry pyridine (1g./10ml.) in a flame-dried round-bottom flask fitted with a dropping funnel to give an intense sienna solution which was chilled in an ice bath to about 5°C. Acetyl chloride (10 equivalents) was added dropwise. After a short time a solid separated and the reaction mixture turned bright yellow. When addition was complete, the cooling bath was removed and the reaction mixture allowed to come to room temperature. The reaction mixture was poured into dilute hydrochloric acid; the off-white solid was triturated, collected, washed thoroughly with dilute hydrochloric acid, and dried to give a pale yellow solid.

The crude tetraacetate was dissolved in methanol (1g./40ml.) and filtered. Dilute alkali was added, and the reaction mixture was stirred 1 hour at room temperature. The intensely blue solution was filtered to remove minor amounts of insoluble materials and the filtrate precipitated into dilute hydrochloric acid. The precipitate was collected, washed and dried and recrystallized from ethyl acetate/hexane to yield the title compound.

#### EXAMPLE 3

Preparation of the compound of formula (14).

Following the procedure of Example 1, 3-hydroxy-3-(4'-hydroxynaphthyl)phthalide was reacted with n-dodecylamine and formalin and then acetylated according to the procedure of Example 2. The intermediate thus obtained was treated with aqueous sodium hydroxide and then reacted with an equivalent of 1-naphthol in the presence of phosphorus oxychloride to yield the title compound.

#### EXAMPLE 4

Preparation of the compound of Formula (1):

Following the procedure of Example 1, analytical grade phenol phthalein was reacted with formalin and n-dodecylamine to yield the title compound.

Each of the indicator dyes prepared in the above examples was coated in a layer of gelatin over another

layer comprising gelatin carried on a support. This element was then superposed with a second element comprising a polymeric layer of polyvinyl alcohol and poly-4-vinylpyridine carried on a transparent support. An aqueous alkaline solution having a pH in excess of about 12 and comprising water, potassium hydroxide and titanium dioxide was spread between the superposed elements. Optical density was measured over a period of about 2 minutes through the transparent support of the second element commencing upon spreading of the aqueous solution to determine whether or not indicator dye was migrating through the layer of aqueous solution to the polymeric layer. The density measurements as measured by reflection at the  $\lambda_{max}$  for each dye revealed that substantially no increase in density occurred during the 2 minute interval indicating that each of the dyes was substantially non-diffusible from its original position in the first element.

As noted above, it has been found that the pKa of the indicator dyes containing  $-CH_2-NRR'$  group(s) wherein R is other than hydrogen, e.g., acetyl, exhibit a higher pKa than those dyes where the R substituent is hydrogen. For example, the pKa value measured for the indicator dye of Example 1 was approximately 7 which is in substantially the same range as the pKa for 1-naphtholphthalein which has two pKa's, one at about 7 and a second at about 8. In comparison, the pKa values measured for the indicator dyes of Examples 2 and 3 were 10.1 and 9.2, respectively. Because of the substantial increase in pKa for dyes of the latter type, such dyes may be rendered colorless at a high pH. Such dyes are particularly useful as optical filter agents in photographic processes, e.g., diffusion transfer processes performed at a comparatively high pH where it is desired to clear the dye relatively rapidly upon reduction of the pH to permit early viewing of the image.

The pH sensitive indicator dyes of the present invention may be used as optical filter agents in any photographic process including conventional tray processing and diffusion transfer photographic techniques. In such processes, the dye or dyes during development of a selectively exposed photosensitive material will be in a position and in a concentration effective to absorb a given level of non-selective radiation incident on and actinic to the photosensitive material. The dyes may be initially disposed in the film unit, for example, in a layer(s) coextensive with one or both surfaces of the photosensitive layer. Where selective exposure of the photosensitive material is made through a layer containing the indicator dye, then the dyes should be in a non-light-absorbing form until the processing solution is applied. Alternately, the dyes may be initially disposed in the processing composition in their light-absorbing form, for example, in the developing bath in tray processing or in the layer of processing solution distributed between the photosensitive element and the superposed image-receiving element (or spreader sheet) in diffusion transfer processing. The particular indicator dye or dyes selected should have an absorption spectrum corresponding to the sensitivity of the photosensitive layer, so as to afford protection over the predetermined wavelength range required by the particular photosensitive material employed and should have a pKa such that they are in their colored form, i.e., light-absorbing form at the pH at which the photographic process is performed. Most commercially useful photographic processes are performed under alka-

line conditions. Diffusion transfer processes, for example, usually employ highly alkaline processing solutions having a pH in excess of 12.

In photographic processes where the optical filter agent is retained in a stratum through which the final image is to be viewed, the color of the indicator dye may be discharged subsequent to image formation by adjusting the pH of the system to a value at which the dye is substantially non-light absorbing in the visible spectrum. In photographic processes performed at an alkaline pH, the optical filter agent, such as, a dye or dyes of the present invention are rendered substantially colorless by reducing the environmental pH. In processes where the optical filter agent is removed or separated from the layer containing the final image or retained in a layer that does not interfere with viewing of the final image, it is unnecessary to convert the indicator dye to its non-light-absorbing form, though the color may be discharged if desired.

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 multi-color 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 one minute in 10,000 foot candles of color corrected light, a light intensity approximating 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 color film units 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.

Since most commercial photographic processes employ photosensitive materials sensitive to and exposable by actinic radiation throughout the visible spectrum, e.g., black-and-white panchromatic silver halide emulsions and multilayer silver halide emulsion elements, it is preferred to use a second dye(s) in conjunction with the subject dye(s) that has a principal absorption in a second and at least partially different predetermined wavelength range such that the combination of dyes will afford protection from non-selective incident actinic radiation over the range of 400 to 700 nm. The second dye employed may be non-color-changing but preferably, is also pH sensitive, i.e., has reversibly alterable spectral absorption characteristics in response to changes in the environmental pH so that it may be ren-

dered light-absorbing or non-light-absorbing as desired. Illustrative of such dyes are phthaleins derived from indoles, such as, indole phthalein. The second dye also may be initially present in the film unit or in the processing composition as discussed above either together with or separate from the subject dyes and subsequent to processing may be removed from the film unit or retained within the film structure, provided it is in a form or position such that it does not interfere with viewing of the image produced.

Dyes may be selected from those described above that are particularly useful as optical filter agents in diffusion transfer processes, for example, those employing composite diffusion transfer photosensitive elements including a film pack or roll wherein superposed photosensitive and image-receiving elements are maintained as a laminate after formation of the final image. Such elements include at least one transparent support to allow viewing of the final image without destroying the structural integrity of the film unit. Preferably, the support carrying the photosensitive layer(s) is opaque and the support carrying the image-receiving layer is transparent and selective photoexposure of the photosensitive layer(s) and viewing of the final image both are effected through the latter support. The final image is viewed as a reflection print, i.e., by reflected light, provided by a reflecting agent initially disposed in the processing composition applied and maintained intermediate the image-receiving and next adjacent photosensitive layer or by a preformed layer of reflecting agent initially positioned intermediate the image-receiving and next adjacent photosensitive layer. It will be understood that a preformed reflecting layer, while it should be capable of masking the photosensitive layer(s) subsequent to image formation, should not interfere with selective photoexposure of the photosensitive material prior to processing.

When utilizing reflection-type composite film units, the indicator dye or dyes employed as the optical filter agent(s) may be positioned initially in a layer of the film unit, e.g., in a layer between the image-receiving and next adjacent photosensitive layer through which photo-exposure is effected provided it is incorporated under conditions, i.e., at a pH such that it will not absorb actinic radiation intended to selectively expose the photosensitive material to form a latent image therein. For example, the optical filter agent may be in a layer coated over either the image-receiving layer or the next adjacent photosensitive layer and should remain substantially non-light-absorbing until a processing composition is applied providing a pH at which the indicator dye is capable of being rapidly converted to its light-absorbing form to provide light protection when the film unit is removed from the camera. Rather than being initially disposed in the film unit, the indicator dye may be initially present in the processing composition applied intermediate the image-receiving and next adjacent photosensitive layer subsequent to photoexposure. The dye, when initially disposed in the processing composition, will be in its light-absorbing form.

The dyes selected as optical filter agents should exhibit at the initial pH of the processing, maximum spectral absorption of radiation at the wavelengths to which the film unit's photosensitive silver halide layer or layers are sensitive, and preferably, should be substantially immobile or non-diffusible in the alkaline processing composition in order to achieve optimum efficiency as



a radiation filter and to prevent diffusion of filter agent into layers of the film unit where its presence may be undesirable. Recognizing that the filter agent absorption will detract from image-viewing characteristics by contaminating reflecting pigment background, the selected agents should be those exhibiting major spectral absorption at the pH at which processing is effected and minimal absorption at a pH below that which obtains during transfer image formation. Accordingly, the selected optical filter agent or agents should possess a pKa below that of the processing pH and above that of the environmental pH subsequent to transfer image formation.

As discussed previously, 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. In the processes where the indicator dye or dyes selected as optical filter agents are used in conjunction with a reflecting agent or agents, the optical filter agents and reflecting agents together should possess the optical transmission density necessary to protect the photosensitive material for the particular photographic process. The optimum concentration of optical filter agent(s) or filter agent(s) together with reflecting agent(s) may be readily determined empirically for each photographic system.

While substantially any reflecting agent may be employed for the layer of reflecting agent, either preformed or applied as a component of the processing composition, it is preferred to select an agent 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 detracting from the information content of the image. Particularly desirable reflecting agents will be those providing a white background, for viewing the transfer image, and specifically those conventionally employed to provide background for reflection photographic prints and, especially, those agents possessing the optical properties desired for reflection of incident radiation.

As examples of reflecting agents, mention may be made of barium sulfate, zinc sulfide, titanium dioxide, barium stearate, silver flake, silicates, alumina, zirconium oxide, zirconium acetyl acetate, sodium zirconium sulfate, kaolin, mica, and the like.

Illustrative of the photographic use of the indicator dyes of the present invention as optical filter agents, a photographic film unit was 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-( $\beta$ -[hydroquinonyl- $\alpha$ -methyl]-ethylamino)-5,8-dihydroxy-anthraquinone dispersed in gelatin and coated at a coverage of about 80 mgs./ft.<sup>2</sup> of dye and about 100 mgs./ft.<sup>2</sup> of gelatin;

2. a red-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 225 mgs./ft.<sup>2</sup> of silver and about 50 mgs./ft.<sup>2</sup> 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 mgs./ft.<sup>2</sup> of AC-61 and about 5 mgs./ft.<sup>2</sup> of polyacrylamide;

4. a layer of the magenta dye developer 2-(p-[ $\beta$ -hydroquinonylethyl]-phenylazo)-4-isopropoxy-1-naphthol dispersed in gelatin and coated at a coverage of 70 mgs./ft.<sup>2</sup> of dye and about 120 mgs./ft.<sup>2</sup> of gelatin;

5. a green-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 120 mgs./ft.<sup>2</sup> of silver and 60 mgs./ft.<sup>2</sup> 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 mgs./ft.<sup>2</sup> of B-15 and about 10 mgs./ft.<sup>2</sup> of polyacrylamide;

7. a layer of the yellow dye developer 4-(p-[ $\beta$ -hydroquinonylethyl]-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 mgs./ft.<sup>2</sup> of dye, about 15 mgs./ft.<sup>2</sup> of auxiliary developer and 50 mgs./ft.<sup>2</sup> of gelatin;

8. a blue-sensitive gelatino-silver iodobromide emulsion coated at a coverage of about 75 mgs./ft.<sup>2</sup> of silver and about 75 mgs./ft.<sup>2</sup> of gelatin; and

9. a layer of gelatin coated at a coverage of about 50 mgs./ft.<sup>2</sup> of gelatin.

Then a transparent 4 mil. polyethylene terephthalate film base was 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 mgs./ft.<sup>2</sup>, to provide a polymeric acid layer;

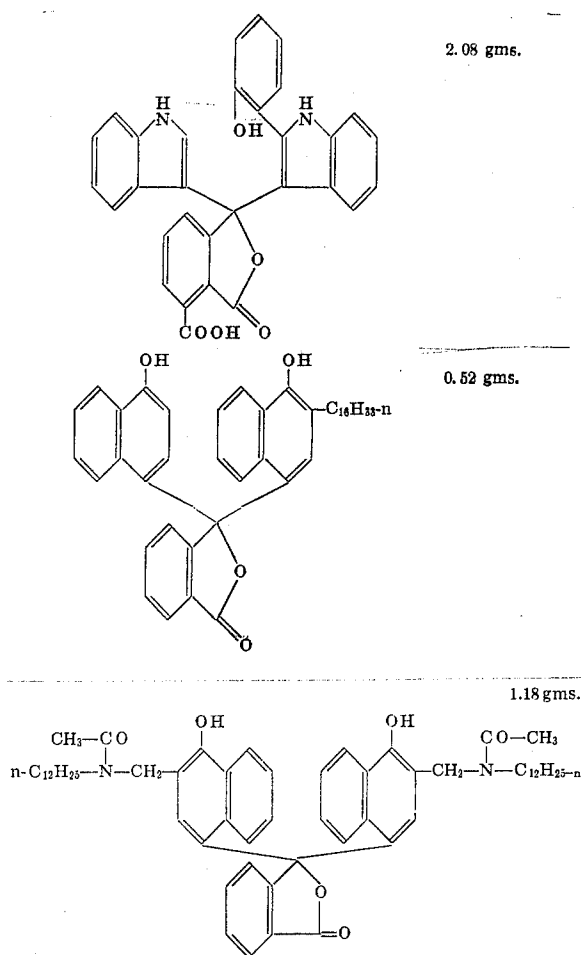
2. a graft copolymer of acrylamide and diacetone acrylamide on a polyvinyl alcohol backbone in a molar ratio of 1:3.2:1 at a coverage of about 800 mgs./ft.<sup>2</sup>, to provide a polymeric spacer layer; and

3. a 2:1 mixture, by weight, of polyvinyl alcohol and poly-4-vinylpyridine, at a coverage of about 900 mgs./ft.<sup>2</sup> and including about 20 mgs./ft.<sup>2</sup> phenyl mercapto tetrazole, to provide a polymeric image-receiving layer.

The two components thus prepared were then 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 gms.
Hydroxyethyl cellulose (high viscosity) [commercially available from Hercules Powder Co., Wilmington, Delaware, under the trade name Natrasol 250]	3.4 gms.
N-phenethyl- $\alpha$ -picolinium bromide	2.7 gms.
Benzotriazole	1.15 gms.
Titanium dioxide	50.0 gms.



was then 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 were 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 the polymeric image-receiving layer and gelatin layer 9 of the photosensitive component. The film unit may be exposed to incident light and the formation of the image may be viewed upon distribution of the processing composition by reason of the protection against incident radiation afforded the photosensitive silver halide emulsion layers by the optical filter agents and by reason of the effective reflective background afforded by the titanium dioxide.

The film unit detailed above is similar to that shown in FIG. 2 and related FIGS. 3 and 4 of aforementioned

copending U. S. Pat. application Ser. No. 101,968. The negative component of the film unit including the photosensitive strata and associated dye-image-forming material; the positive component including the timing, neutralizing and dyeable layers; and the processing composition including its components, such as, the alkaline material and various addenda are described in detail in application Ser. No. 101,968. For convenience, the specification of this application is specifically incorporated herein.

Besides the above photosensitive element, dyes of the present invention may be employed in composite photosensitive elements, in general, where the dyeable stratum along with any associated layers may be contained together with the photosensitive strata as a unitary film unit which may be termed an integral negative-positive film unit comprising a negative component including the aforementioned essential layers and a positive component including at least the dyeable stratum in which the color transfer image is to be formed. The essential layers are preferably contained on a transparent dimensionally stable layer or support member positioned closest to the dyeable stratum so that the resulting transfer image is viewable through this transparent layer. Most preferably another dimensionally stable layer which may be transparent or opaque is positioned on the opposed surface of the essential layers so that the aforementioned essential layers are sandwiched or confined between a pair of dimensionally stable layers or support members, at least one of which is transparent to permit viewing therethrough of a color transfer image obtained as a function of development of the exposed film unit in accordance with the known color diffusion transfer processes. It will be appreciated that all of these film units, like the specific one detailed above, may optionally contain other layers performing specific desired functions, e.g., spacer layers, pH-reducing layers, etc.

As examples of such integral negative-positive film units for preparing color transfer images viewable without separation are those described and claimed in aforementioned U. S. Pat. No. 3,415,644 and in U. S. Pat. Nos. 3,415,645, 3,415,646, 3,473,925, and 3,573,043; as well as those described in copending application Ser. No. 65,084, filed Aug. 19, 1970, in the name of Edwin H. Land, now U.S. Pat. No. 3,672,890; and Ser. Nos. 39,646 and 39,666 of Howard G. Rogers, filed May 22, 1970 and now U. S. Pat. Nos. 3,594,165 and 3,594,164, respectively.

In general, the film units of the foregoing description, e.g., those described in the aforementioned patents and/or copending applications, are exposed to form a developable image and thereafter developed by applying the appropriate processing composition to develop exposed silver halide and to form, as a function of development, an imagewise distribution of diffusible dye image-providing material which is transferred, at least in part by diffusion, to the dyeable stratum to impart thereto the desired color transfer image, e.g., a positive color transfer image. Common to all of these systems is the provision of a reflecting layer between the dyeable stratum and the photosensitive strata to mask effectively the latter and to provide a background for viewing the color image contained in the dyeable stratum, whereby this image is viewable without separation, from the other layers or elements of the film unit. As discussed previously, this reflecting layer is pro-

vided prior to photoexposure, e.g., as a preformed layer included in the essential layers of the laminar structure comprising the film unit, and in others it is provided at some time thereafter, e.g., by including a suitable light-reflecting agent, for example, a white pigment, such as titanium dioxide, in the processing composition. As an example of such a preformed layer, mention may be made of that disclosed in the copending applications of Edwin H. Land, Ser. Nos. 846,441, filed July 31, 1969, now U.S. Pat. No. 3,615,421 and 3,645, filed Jan. 19, 1970 now U.S. Pat. No. 3,620,724. The reflecting pigment may be generated in situ as is disclosed in the copending applications of Edwin H. Land, Ser. Nos. 43,741 and 43,742, both filed June 5, 1970 and now U.S. Pat. Nos. 3,647,434 and 3,647,435, respectively. In a particularly preferred form, such film units are employed in conjunction with a rupturable container, such as, that used above, containing the processing composition having the light-reflecting agent incorporated therein which container is adapted upon application of pressure of distributing its contents to develop the exposed film unit and to provide the light-reflecting layer.

As noted previously, the photographic use of the dyes of the present invention as optical filter agents to prevent post-exposure fogging of a selectively exposed photo-sensitive material is not limited to diffusion transfer processes nor to such processes employing composite photo-sensitive elements. While the use of such dyes in composite multicolor diffusion transfer film units is a particularly preferred embodiment of the present invention, these dyes may be used with equally effective results in any photographic process where it is desired to protect a photosensitive material from incident radiation actinic to the photosensitive material within the wavelength range capable of being absorbed by the dye. For example, the subject dyes may be used in conventional tray photographic processing as a component of the processing bath, or they may be present in a layer coextensive with one or both surfaces of a layer of photo-sensitive material to be processed using conventional tray procedures, provided that they are non-light-absorbing prior to photoexposure and also subsequent to developing the latent image unless the layer containing the dye is to be removed subsequent to processing. In such procedures, the photo-exposed photosensitive material will, of course, be transferred from the camera to the processing bath in the absence of radiation actinic to the material.

The subject dyes also may be employed in diffusion transfer processes where the photosensitive and image-receiving elements are separated subsequent to the formation of a transfer image or where a spreader sheet is separated from the photosensitive element to reveal a final image in the negative. In addition to the composite diffusion transfer structures described above, the subject dyes may be used with composite diffusion transfer film units where the final image is to be viewed by transmitted light. Also they may be used in composite film units specifically adapted, for example, for forming a silver transfer image, for developing a negative silver image by monobath processing, for obtaining an additive color image, and for obtaining a dye image by the silver dye bleach process which structures are described in detail in aforementioned copending U. S. application Ser. No. 101,968, particularly with reference to FIGS. 10 to 13 of the application's drawings.

In view of the foregoing, it will be readily apparent that the subject dyes are useful generally in photo-

graphic processes for producing silver, monochromatic and multi-color images using any photosensitive material including conventional and direct positive silver halide emulsions. Depending upon the selected photosensitive material, one or more of the dyes may be used alone or in combination with another optical filter agent, such as another light-absorbing dye, which second dye may be non-color-changing or another pH sensitive dye. If the selected dye or dyes do not possess the desired stability in the processing composition for long term storage therein, they may be initially disposed in the film structure or stored in a double-compartmented pod or in one of two associated pods separate from the processing solution until such time as the pod(s) are ruptured whereupon the dyes are admixed with the processing solution.

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 shall be interpreted as illustrative and not in a limiting sense.

What is claimed:

1. 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 a processing composition to provide an indicator dye in a form capable of absorbing a predetermined wavelength range of radiation actinic to said photosensitive material, and developing said latent image while exposing said photosensitive element non-selectively to incident actinic radiation within said predetermined wavelength range, said indicator dye being present during development in a position and quantity effective to absorb said wavelength range of incident radiation in an amount sufficient to prevent any substantial increase, as a result of performing said process in the presence of incident radiation within said wavelength range, in the minimum density of the image obtained by said development of said latent image, and being selected from a 3,3-disubstituted phthalide and a 3,3-disubstituted naphthalide wherein the 3,3 substituents are p-hydroxycarbocyclic aryl radicals, at least one of said radicals possessing a  $-CH_2-NRR'$  group ortho to the p-hydroxy group wherein said R is hydrogen, alkyl, aryl or acyl and said R' is alkyl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-CH_2-NRR'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution.

2. A process as defined in claim 1 wherein said indicator dye is initially disposed in said processing composition having a pH at which said indicator dye is light-absorbing, said processing composition being applied to said photosensitive layer and said composition containing said indicator dye being separated from the photosensitive layer subsequent to substantial image development.

3. A process as defined in claim 1 wherein said indicator dye is retained in said element and is rendered ineffective to prevent viewing of the final image subsequent to substantial image development by adjusting the pH of said indicator dyes environment to a value at which it is substantially non-light-absorbing.

4. A process as defined in claim 3 wherein said indicator dye is initially present in a processing composition permeable layer at a pH value at which it is sub-

stantially non-light absorbing, said layer being coextensive with at least one surface of said photosensitive layer and said processing composition applied thereto having a pH at which said indicator dye is light-absorbing.

5 5. A process as defined in claim 1 wherein said layer of photosensitive material is a silver halide layer.

6. A process as defined in claim 1 wherein said indicator dye is a phthalide.

7. A process as defined in claim 6 wherein said carbocyclic aryl radicals are p-hydroxyphenyl radicals.

8. A process as defined in claim 7 wherein both of said radicals are substituted with  $-CH_2-NRR'$  groups, the same.

9. A process as defined in claim 8 wherein  $R'$  is alkyl.

10. A process as defined in claim 9 wherein  $R$  is hydrogen.

11. A process as defined in claim 6 wherein said carbocyclic aryl radicals are p-hydroxynaphthyl radicals.

12. A process as defined in claim 11 wherein one of said radicals is substituted with a  $-CH_2-NRR'$  group.

13. A process as defined in claim 12 wherein  $R'$  is alkyl.

14. A process as defined in claim 13 wherein  $R$  is acyl.

15. A process as defined in claim 11 wherein both of said radicals are substituted with  $-CH_2-NRR'$  groups, the same.

16. A process as defined in claim 15 wherein  $R'$  is alkyl.

17. A process as defined in claim 16 wherein  $R$  is hydrogen.

18. A process as defined in claim 15 wherein  $R$  is acyl.

19. A process as defined in claim 9 wherein  $R'$  is n-dodecyl.

20. A process as defined in claim 19 wherein  $R$  is hydrogen.

21. A process as defined in claim 13 wherein  $R'$  is n-dodecyl.

22. A process as defined in claim 21 wherein  $R$  is acetyl.

23. A process as defined in claim 16 wherein  $R'$  is n-dodecyl.

24. A process as defined in claim 23 wherein  $R$  is hydrogen.

25. A process as defined in claim 23 wherein  $R$  is acetyl.

26. A process of forming photographic diffusion transfer images which comprises, in combination, the steps of:

a. exposing a photographic film unit which comprises a plurality of layers including an opaque support layer carrying a photosensitive silver halide layer having associated therewith a compound capable of providing as a function of development an imagewise distribution of an image-forming material which is processing composition soluble and diffusible as a function of the point-to-point degree of exposure of said silver halide layer and a diffusion transfer process image-receiving layer adapted to receive solubilized image-forming material diffusing thereto;

b. contacting said photosensitive silver halide layer with an aqueous alkaline processing composition to provide an indicator dye in a form capable of absorbing a predetermined wavelength range of radi-

ation actinic to said photosensitive material, said indicator dye being selected from a 3,3-disubstituted phthalide and a 3,3-disubstituted naphthalide wherein said 3,3 substituents are p-hydroxycarbocyclic aryl radicals, at least one of said radicals possessing a  $-CH_2-NRR'$  group ortho to the p-hydroxy group wherein said  $R$  is hydrogen, alkyl, aryl or acyl and said  $R'$  is alkyl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-CH_2-NRR'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution;

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

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

e. transferring, by diffusion, at least a portion of said imagewise distribution of diffusible image-forming material to said layer adapted to receive said material to provide an image therein; said indicator dye being present during development in a position and quantity effective to absorb said wavelength range of actinic radiation in an amount sufficient to prevent any substantial decrease, as a result of performing said process in the presence of incident actinic light within said wavelength range, in the maximum density of the image obtained by the transfer of said diffusible image-forming material.

27. A process of forming transfer images as defined in claim 26 wherein said indicator dye is disposed, at a pH below its pKa, in a separate processing composition permeable layer and said photosensitive silver halide layer is positioned intermediate said opaque support and said layer containing said indicator dye.

28. A process of forming transfer images in color which comprises, in combination, the steps of:

a. exposing a photographic film unit which is adapted to be processed by application of pressure to release and distribute a processing composition and which includes, in combination, a photosensitive element comprising a composite structure containing, as essential layers, in sequence, a first support layer opaque to incident actinic radiation; a photosensitive silver halide layer having associated therewith a compound capable of providing as a function of development an imagewise distribution of a dye image-forming material which is processing composition soluble and diffusible as a function of exposure of the photosensitive silver halide layer to actinic radiation; a polymeric layer dyeable by said dye image-forming material; a second support layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship; means for interposing a reflecting agent and an indicator dye capable of absorbing incident radiation within a predetermined wavelength range actinic to said photosensitive layer at a pH above its pKa intermediate said dyeable polymeric layer and said photosensitive silver halide layer and associated dye image-forming material subsequent to photoexposure of said film unit, said indicator dye being selected from a 3,3-disubstituted phthalide and a 3,3-disubstituted naphthalide wherein said 3,3 substituents are p-hydroxycarbocyclic aryl rad-

icals, at least one of said radicals possessing a  $-\text{CH}_2-\text{NRR}'$  group ortho to the p-hydroxy group wherein said R is hydrogen, alkyl, aryl or acyl and said R' is aryl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-\text{CH}_2-\text{NRR}'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution;

- b. rupturable container retaining an aqueous alkaline processing composition possessing a pH above the pKa of said indicator dye fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of the container's processing composition intermediate said dyeable polymeric layer and the photosensitive silver halide layer next adjacent thereto upon application of compressive force to said container;
- c. applying compressive force to said rupturable container to effect unidirectional discharge of the container's processing composition intermediate said dyeable polymeric layer and said photosensitive silver halide layer;
- d. effecting thereby substantial development of said silver halide layer and disposition of said reflecting agent and said indicator dye at a pH above its pKa intermediate said dyeable polymeric layer and said photosensitive silver halide layer;
- e. as a result of said development, forming an image-wise distribution of diffusible dye image-forming material, as a function of the point-to-point degree of exposure of said photosensitive layer;
- f. transferring, by diffusion, at least a portion of said imagewise distribution of diffusible dye image-forming material to said dyeable polymeric layer to provide a dye image thereto; and
- g. maintaining said composite structure intact subsequent to said processing, said indicator dye being present in a quantity effective to absorb said wavelength range of incident radiation in an amount sufficient in combination with said reflecting agent, to prevent any substantial decrease, as a result of performing said process in the presence of incident actinic light within said wavelength range, in the maximum density of the image obtained by the transfer of said diffusible image-forming material.

29. A process of forming transfer images in color as defined in claim 28 wherein said indicator dye is initially disposed at a pH below its pKa in an aqueous alkaline processing composition permeable layer of said photosensitive element intermediate said dyeable polymeric layer and said silver halide layer, and said rupturable container containing said aqueous alkaline processing composition possessing a pH above the pKa of said indicator dye is fixedly positioned and extends transverse a leading edge of said photosensitive element to effect unidirectional discharge of the processing composition said indicator dye upon application of compressive force to said container and including the step of discharging said processing composition, subsequent to exposure of said photosensitive element, intermediate said dyeable polymeric layer and said layer containing said indicator dye.

30. A process of forming transfer images in color as defined in claim 28 wherein said reflecting agent is titanium dioxide and said indicator dye and said titanium dioxide are initially disposed in said aqueous alkaline

processing composition as retained in said rupturable container.

31. A process of forming transfer images in color as defined in claim 28 wherein said photosensitive element includes at least one acid reacting polymeric layer positioned intermediate at least one of (a) said first opaque layer and the photosensitive silver halide layer next adjacent thereto, and (b) said second transparent layer and the dyeable polymeric layer next adjacent thereto, and contains sufficient acidifying function to effect reduction of said aqueous alkaline processing composition from a pH above to a pH below the pKa of said indicator dye and including the step of transferring, by diffusion, subsequent to substantial transfer dye image formation, a sufficient portion of the ions of said processing composition to said polymeric acid layer to thereby reduce said pH to a pH below said pKa.

32. A process of forming transfer images in color as defined in claim 31 wherein said dye-image forming material comprises a dye which is a silver halide developing agent and said photosensitive layer is a silver halide emulsion.

33. A process of forming transfer images in color as defined in claim 32 wherein said photosensitive element comprises at least two selectively sensitized silver halide emulsion layers, each of said layers having associated therewith an image-forming dye, which is a silver halide developing agent, of predetermined color, and is soluble and diffusible, in aqueous alkaline processing composition as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

34. A process of forming transfer images in color as defined in claim 28 wherein said photosensitive element comprises three selectively sensitized silver halide emulsion layers on said support, in sequence, a red-sensitive silver halide emulsion layer having associated therewith a cyan image-forming dye; a green-sensitive silver halide emulsion layer having associated therewith a magenta image-forming dye; a blue-sensitive silver halide emulsion layer having associated therewith a yellow image-forming dye; each of said cyan, magenta and yellow image-forming dyes being silver halide developing agents and soluble and diffusible in said aqueous alkaline processing solution.

35. A process as defined in claim 28 wherein said dye is a phthalide.

36. A process as defined in claim 35 wherein said carbocyclic aryl radicals are p-hydroxyphenyl radicals.

37. A process as defined in claim 36 wherein both of said radicals are substituted with  $-\text{CH}_2-\text{NRR}'$  groups, the same.

38. A process as defined in claim 37 wherein R' is alkyl.

39. A process as defined in claim 38 wherein R is hydrogen.

40. A process as defined in claim 35 wherein said carbocyclic aryl radicals are p-hydroxynaphthyl radicals.

41. A process as defined in claim 40 wherein one of said radicals is substituted with a  $-\text{CH}_2-\text{NRR}'$  group.

42. A process as defined in claim 41 wherein R' is alkyl.

43. A process as defined in claim 42 wherein R is acyl.

44. A process as defined in claim 40 wherein both of said radicals are substituted with  $-\text{CH}_2-\text{NRR}'$  groups, the same.

45. A process as defined in claim 44 wherein R' is alkyl.
46. A process as defined in claim 45 wherein R is hydrogen.
47. A process as defined in claim 45 wherein R is acyl.
48. A process as defined in claim 38 wherein R' is n-dodecyl.
49. A process as defined in claim 48 wherein R is hydrogen.
50. A process as defined in claim 42 wherein R' is n-dodecyl.
51. A process as defined in claim 59 wherein R is acetyl.
52. A process as defined in claim 45 wherein R' is n-dodecyl.
53. A process as defined in claim 52 wherein R is hydrogen.
54. A process as defined in claim 52 wherein R is acetyl.
55. A photographic film unit which comprises a plurality of layers including a support layer carrying on one surface, in order, a layer of photosensitive material and a layer comprising an indicator dye disposed at a pH below its pKa selected from a 3,3-disubstituted phthalide and a 3,3-disubstituted naphthalide wherein said 3,3 substituents are p-hydroxycarbocyclic aryl radicals, at least one of said radicals possessing a  $-\text{CH}_2-\text{NRR}'$  group ortho to the p-hydroxy group wherein said R is hydrogen, alkyl, aryl or acyl and said R' is alkyl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-\text{CH}_2-\text{NRR}'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution.
56. A photographic film unit as defined in claim 58 wherein said photosensitive material is silver halide.
57. A photographic film unit as defined in claim 56 wherein said silver halide layer has associated therewith a silver halide developing agent.
58. A photographic film unit as defined in claim 56 wherein said silver halide layer has associated therewith a dye-providing compound capable of providing as a function of development an imagewise distribution of a dye image-forming material which is processing composition soluble and diffusible as a function of the point-to-point degree of exposure of said silver halide layer.
59. A photographic film unit as defined in claim 58 which is adapted to be processed by application of pressure to release and distribute a processing composition and which comprises, in combination:
- a photosensitive element including a composite structure containing, as essential layers, in sequence, a first support layer opaque to incident actinic radiation; at least two selectively sensitized silver halide layers, each having associated therewith an image-forming dye which is a silver halide developing agent of predetermined color, each of said dyes being soluble and diffusible in alkaline processing composition as a function of the point-to-point degree of exposure of the respective silver halide associated therewith, a polymeric layer dyeable by said dye; a second support layer transparent to incident actinic radiation; and means securing said layers in substantially fixed relationship;

- a rupturable container retaining an alkaline processing composition containing reflecting agent fixedly positioned and extending transverse a leading edge of said photosensitive element to effect unidirectional discharge of said container's processing composition between said dyeable polymeric layer and the photosensitive silver halide layer next adjacent thereto upon application of pressure to said container; and an indicator dye capable of absorbing incident radiation within a predetermined wavelength range actinic to said silver halide disposed in at least one of said processing composition and, at a pH below its pKa, in a layer intermediate said photosensitive silver halide layer and said second support layer transparent to incident actinic radiation, said indicator dye being selected from a 3,3-substituted phthalide, and a 3,3-disubstituted naphthalide wherein said 3,3 substituents are p-hydroxycarbocyclic aryl radicals, at least one of said radicals possessing a  $-\text{CH}_2-\text{NRR}'$  group ortho to the p-hydroxy group wherein said R is hydrogen, alkyl, aryl or acyl and said R' is alkyl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-\text{CH}_2-\text{NRR}'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution.
60. A photographic film unit as defined in claim 59 including at least one acid reacting polymeric layer positioned intermediate at least one of said first opaque layer and the photosensitive silver halide layer next adjacent thereto, and said second transparent layer and the dyeable polymeric layer next adjacent thereto, said polymeric acid layer containing sufficient acidifying function to effect reduction of said processing composition from a first pH at which said image-forming dye is substantially soluble and diffusible to a second pH at which said dye is substantially nondiffusible.
61. A photographic film unit as defined in claim 60 wherein said reflecting agent taken together with said indicator dye are adapted to prevent further exposure of the selectively exposed silver halide layer during processing in the presence of radiation within said predetermined wavelength range actinic to the silver halide layer and incident on the surface of the film unit opposite to the opaque support layer.
62. A photographic film unit as defined in claim 61 wherein said photosensitive element includes, as essential layers, in sequence, from said opaque support layer, an alkaline solution permeable polymeric layer containing a cyan dye; a red-sensitive silver halide emulsion layer; and alkaline solution permeable polymeric layer containing a magenta dye; a green-sensitive silver halide emulsion layer; an alkaline solution permeable polymeric layer containing a yellow dye; a blue-sensitive silver halide emulsion layer, each of said cyan, magenta and yellow dyes being silver halide developing agents and being soluble and diffusible, in aqueous alkaline solution at said first pH and substantially insoluble in aqueous alkaline solution at said second pH.
63. A film unit as defined in claim 55 wherein said dye is a phthalide.
64. A film unit as defined in claim 63 wherein said carbocyclic aryl radicals are p-hydroxyphenyl radicals.
65. A film unit as defined in claim 64 wherein both

of said radicals are substituted with  $-\text{CH}_2\text{-NRR}'$  groups, the same.

66. A film unit as defined in claim 65 wherein  $\text{R}'$  is alkyl.

67. A film unit as defined in claim 66 wherein  $\text{R}$  is hydrogen.

68. A film unit as defined in claim 63 wherein said carbocyclic aryl radicals are p-hydroxynaphthyl radicals.

69. A film unit as defined in claim 68 wherein one of said radicals is substituted with a  $-\text{CH}_2\text{-NRR}'$  group.

70. A film unit as defined in claim 67 wherein  $\text{R}'$  is alkyl.

71. A film unit as defined in claim 70 wherein  $\text{R}$  is acyl.

72. A film unit as defined in claim 68 wherein both of said radicals are substituted with  $-\text{CH}_2\text{-NRR}'$  groups, the same.

73. A film unit as defined in claim 72 wherein  $\text{R}'$  is alkyl.

74. A film unit as defined in claim 73 wherein  $\text{R}$  is hydrogen.

75. A film unit as defined in claim 73 wherein  $\text{R}$  is acyl.

76. A film unit as defined in claim 66 wherein  $\text{R}'$  is n-dodecyl.

77. A film unit as defined in claim 76 wherein  $\text{R}$  is hydrogen.

78. A film unit as defined in claim 70 wherein  $\text{R}'$  is n-dodecyl.

79. A film unit as defined in claim 78 wherein  $\text{R}$  is acetyl.

80. A film unit as defined in claim 78 wherein  $\text{R}'$  is n-dodecyl.

81. A film unit as defined in claim 80 wherein  $\text{R}$  is hydrogen.

82. A film unit as defined in claim 80 wherein  $\text{R}$  is acetyl.

83. A photographic processing composition comprising an aqueous alkaline solution of a viscosity imparting reagent, a light reflecting agent and an indicator dye selected from a 3,3-disubstituted phthalide and a 3,3-disubstituted naphthalide wherein said 3,3 substituents are p-hydroxycarbocyclic aryl radicals, at least one of said radicals possessing a  $-\text{CH}_2\text{-NRR}'$  group ortho to the p-hydroxy group wherein said  $\text{R}$  is hydrogen, alkyl, aryl or acyl and said  $\text{R}'$  is alkyl, aryl or alkaryl, said carbocyclic aryl radicals being selected from two p-hydroxyphenyl radicals and two p-hydroxynaphthyl radicals and said  $-\text{CH}_2\text{-NRR}'$  group or groups being capable of rendering said dye substantially non-diffusible in aqueous solution.

84. A composition as defined in claim 83 which additionally contains a silver halide developing agent.

85. A composition as defined in claim 83 wherein said dye is a phthalide.

86. A composition as defined in claim 85 wherein said carbocyclic aryl radicals are p-hydroxyphenyl radicals.

87. A composition as defined in claim 86 wherein both of said radicals are substituted with  $-\text{CH}_2\text{-NRR}'$  groups, the same.

88. A composition as defined in claim 87 wherein  $\text{R}'$  is alkyl.

89. A composition as defined in claim 88 wherein  $\text{R}$  is hydrogen.

90. A composition as defined in claim 85 wherein said carbocyclic aryl radicals are p-hydroxynaphthyl radicals.

91. A composition as defined in claim 90 wherein one of said radicals is substituted with a  $-\text{CH}_2\text{-NRR}'$  group.

92. A composition as defined in claim 91 wherein  $\text{R}'$  is alkyl.

93. A composition as defined in claim 92 wherein  $\text{R}$  is acyl.

94. A composition as defined in claim 90 wherein both of said radicals are substituted with  $-\text{CH}_2\text{-NRR}'$  groups, the same.

95. A composition as defined in claim 94 wherein  $\text{R}'$  is alkyl.

96. A composition as defined in claim 95 wherein  $\text{R}$  is hydrogen.

97. A composition as defined in claim 95 wherein  $\text{R}$  is acyl.

98. A composition as defined in claim 88 wherein  $\text{R}'$  is n-dodecyl.

99. A composition as defined in claim 98 wherein  $\text{R}$  is hydrogen.

100. A composition as defined in claim 92 wherein  $\text{R}'$  is n-dodecyl.

101. A composition as defined in claim 100 wherein  $\text{R}$  is acetyl.

102. A composition as defined in claim 95 wherein  $\text{R}'$  is n-dodecyl.

103. A composition as defined in claim 102 wherein  $\text{R}$  is hydrogen.

104. A composition as defined in claim 102 wherein  $\text{R}$  is acetyl.

105. A composition as defined in claim 83 wherein said aqueous alkaline solution has a pH above the pKa of said indicator dye.

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[54] **PHOTOGRAPHIC PROCESSES AND PRODUCTS EMPLOYING 5-HYDROXY-4-AZAPHENANTHRENYL PHTHALEINS AS OPTICAL FILTER AGENTS**

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[58] **Field of Search**..... 96/3, 29 D, 84 R

[57] **ABSTRACT**

This invention relates to a class of phthalein indicator dyes useful as optical filter agents in photographic processes to protect a selectively exposed photosensitive material from further exposure during processing in the presence of incident light. Such dyes comprise 3,3-disubstituted phthalides and 3,3-disubstituted naphthalides wherein the 3,3 substituents are para-hydroxy polycyclic aryl radicals possessing a nitrogen atom included in the ring system adjacent to the para-hydroxy group.

[56] **References Cited**

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**45 Claims, No Drawings**



