United States Patent [19]

Staples

[11] **3,923,510**

[45] **Dec. 2, 1975**

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[54] **PROCESS FOR PRODUCING COLOR IMAGES BY BLEACHING REDOX DIFFUSIBLE DYE RELEASERS**

[75] Inventor: **Jon T. Staples**, Pittsford, N.Y.

[73] Assignee: **Eastman Kodak Company**, Rochester, N.Y.

[22] Filed: **Dec. 6, 1973**

[21] Appl. No.: **422,390**

[52] **U.S. Cl.** .... **96/20**; 96/3 UX; 96/29 D UX; 96/53; 96/54; 96/60 BF UX

[51] **Int. Cl.**^{2}.. **G03C 7/16**; G03C 7/00; G03C 5/54; G03C 5/32

[58] **Field of Search** .... 96/54, 53, 3, 29 D, 20, 96/60 BF, 61 R, 60 R

[56] **References Cited**

UNITED STATES PATENTS

351,673	1/1975	Fleckenstein et al.	96/3
2,728,290	12/1955	Marriage et al.	96/53
3,443,940	5/1969	Bloom et al.	96/3
3,498,787	3/1970	Wilson et al.	96/53
3,503,741	3/1970	Wilson et al.	96/53
3,698,897	10/1972	Gompf et al.	96/3
3,725,062	4/1973	Anderson et al.	96/3
3,734,726	5/1973	Figueras et al.	96/54

Primary Examiner—Charles L. Bowers, Jr.
Assistant Examiner—Richard L. Schilling
Attorney, Agent, or Firm—H. E. Cole

[57] **ABSTRACT**

Color images are prepared by silver-dye bleach processing of a photosensitive element comprising a nondiffusible redox dye releaser such as a p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible dye such as an azo dye.

20 Claims, No Drawings

PROCESS FOR PRODUCING COLOR IMAGES BY BLEACHING REDOX DIFFUSIBLE DYE RELEASERS

This invention relates to photography, and more particularly to color photography employing dye image-providing materials comprising nondiffusible redox dye releasers such as p-sulfonamidoanilines and p-sulfonamidophenols which are alkalicleavable upon oxidation to release a diffusible, bleachable dye, such as an azo dye from the benzene nucleus. A silver-dye bleach bath is employed with such materials in order to produce color images, such as positive transparency or a motion-picture film.

The silver-dye bleach process has been known for many years. Such a process employs a photographic material comprising at least one photosensitive silver halide emulsion layer which is associated with a preformed bleachable dye. A typical multicolor silver-dye bleach element is composed of three silver halide layers respectively sensitized to red, green, and blue radiation, and having associated therewith, respectively, a bleachable cyan, magenta and yellow dye. The processing such an element for obtaining a positive multicolored photographic reproduction generally includes exposing said element to a light pattern, developing it to a negative silver image in a black-and-white silver halide developer solution, treating it in a dye bleach bath which oxidizes the silver image to a silver salt and concurrently decolorizes the associated pattern of dye, and, finally removing the residual silver salt by fixing and washing. A dye image is left which is photographically the inverse of the initial silver image. General descriptions of this well known silver-dye bleach process are found in U.S. Pat. No. 3,498,787 of Wilson et al, issued Mar. 3, 1970; U.S. Pat. No. 3,414,411 of Michel et al, issued Dec. 3, 1968; U.S. Pat. No. 3,503,741 of Wilson et al, issued Mar. 31, 1970; Canadian Pat. No. 790,533 of Wilson et al, issued July 23, 1968; and an article entitled "Some Features of the Silver-Dye Bleach Process" by A. Meyer, *The Journal of Photographic Science*, Volume 13, 90–97 (1965); the disclosures of which are hereby incorporated by reference.

Copending U.S. application Ser. No. 351,673 of Fleckenstein et al, filed Apr. 16, 1973; Fleckenstein U.S. application Ser. No. 351,700 filed Apr. 16, 1973; U.S. application Ser. No. 331,727 of Landholm et al filed Feb. 12, 1973, now abandoned; U.S. application Ser. No. 331,728 of Haase et al filed Feb. 12, 1973, now abandoned; and U.S. application Ser. No. 331,729 of Landholm et al filed Feb. 12, 1973, now abandoned, relate to various nondiffusible p-sulfonamidoanilines and p-sulfonamidophenols and their use in photographic elements containing such compounds. In a preferred embodiment of my invention, I have found that a color image, such as a positive transparency, may be obtained by employing certain of these compounds in photographic elements which are subjected to a silver-dye bleach process.

There is a disclosure in the above-mentioned Fleckenstein et al application Ser. No. 351,673, of obtaining a color transparency by treating the residual dye image in a photographic element after an imagewise distribution of dye has diffused out of the element. There is no disclosure in this application, however, of employing a silver-dye bleach bath which I have found greatly enhances the color image which is obtained. This is especially noticeable in greatly improved D_{mins} which are obtained in accordance with the present invention.

It is therefore an object of this invention to provide a process for producing an improved color image employing a photosensitive element containing a nondiffusible redox dye releaser.

It is another object of this invention to provide a process for producing an improved color image employing a photosensitive element containing a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible dye.

It is still another object of this invention to provide a process for obtaining a color image by employing a silver-dye bleach step with photographic elements containing nondiffusible redox dye releasers such as p-sulfonamidoanilines or p-sulfonamidophenols.

These and other objects are achieved by my invention which is described hereinafter.

According to my invention, a process for producing a color image comprises:

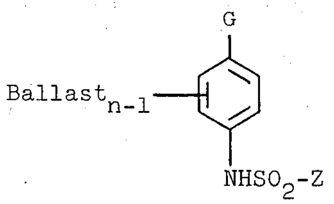
I. imagewise exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, the emulsion layer having associated therewith a nondiffusible redox dye releaser;
II. treating the photosensitive element with an alkaline processing composition in the presence of a silver halide developing agent to effect development of each of the exposed silver halide emulsion layers, thereby oxidizing the developing agent and forming a metallic silver image;
  a. the oxidized developing agent thereby cross-oxidizing the redox dye releaser;
  b. the oxidized redox dye releaser then cleaving, thus forming an imagewise distribution of diffusible dye which diffuses out of said element;
III. bleaching the element to decolorize or destroy any imagewisereleased dye which has not diffused out of said element; and
IV. removing the metallic silver halide from the element;

whereby a dye image is obtained in the element which is the reverse of said metallic silver image.

The nondiffusible redox dye releasers useful in my invention are, generally speaking, compounds which will redox with oxidized developing agent to release a dye, such as by alkaline hydrolysis. Such redox dye releasers are described in U.S. Pat. No. 3,725,062 of Anderson and Lum, issued Apr. 3, 1973; U.S. Pat. No. 3,698,897 of Gompf and Lum, issued Oct. 17, 1972; U.S. Pat. No. 3,628,952 of Puschel et al, issued Dec. 21, 1971; U.S. Pat. No. 3,443,939 of Bloom et al, Issued May 13, 1969; U.S. Pat. 3,443,940 of Bloom et al issued May 13, 1969; and the following copending application Ser. Nos. 351,673 of Fleckenstein et al filed Apr. 16, 1973; 351,700 of Fleckenstein filed Apr. 16, 1973; 331,727 and 331,729 of Landholm et al filed Feb. 12, 1973; and 331,728 of Haase et al filed Feb. 12, 1973.

In an especially preferred embodiment of my invention, a process for producing a color image comprises:

I. imagewise exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, the emulsion layer having associated therewith a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible dye from the benzene nucleus and having the formula:



wherein:

a. Z is a bleachable dye having a predominant spectral absorption within the region of the visible spectrum to which the associated silver halide emulsion is sensitive to a dye precursor;

b. Ballast is an organic ballasting radical of such molecular size and configuration (e.g., simple organic groups or polymeric groups) as to render the sulfonamido compound nondiffusible during development in an alkaline processing composition;

c. G is OR or NHR$_1$ wherein R is hydrogen or a hydrolyzable moiety and R$_1$ is a hydrogen or a substituted or unsubstituted alkyl group of 1 to 22 carbon atoms, such as methyl, ethyl, hydroxyethyl, propyl, butyl, secondary butyl, tert-butyl cyclopropyl, 4-chlorobutyl, cyclobutyl, 4-nitroamyl, hexyl, cyclohexyl, octyl, decyl, octadecyl, dodecyl, benzyl, phenethyl, etc., (when R$_1$ is an alkyl group of greater than 6 carbon atoms, it can serve as a partial or sole Ballast group); and

d. n is a positive integer of 1 to 2 and is 2 when G is OR or when R$_1$ is hydrogen or an alkyl group of less than 8 carbon atoms;

II. treating the photosensitive element with an alkaline processing composition in the presence of a silver halide developing agent to: 1) cause any dye precursor present to become a dye having a predominant spectral absorption within the region of the visible spectrum to which the associated sivler halide emulsion is sensitive, the dye being bleachable; and 2) to effect development of each of the exposed silver halide emulsion layers, thereby oxidizing the developing agent and forming a metallic silver image;

a. the oxidized developing agent thereby cross-oxidizing the sulfonamido compound;

b. the oxidized sulfonamido compound then cleaving, thus forming an imagewise distribution of diffusible dye which diffuses out of the element;

III. bleaching the element to decolorize or destroy an imagewise-released dye which has not diffused out of said element and

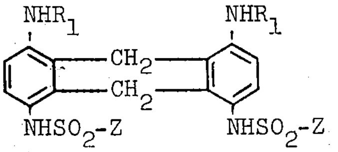
IV. removing the metallic silver and silver halide from the element;

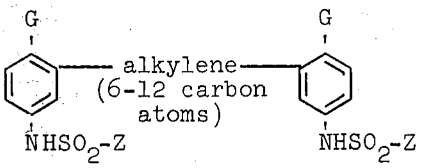
whereby a dye image is obtained in the element which is the reverse of the metallic silver image.

The photosensitive element in the above-described processes can be treated with an alkaline processing composition to effect or initiate development in any manner. A preferred method for applying processing composition is by employing a bath which contains the composition. The alkaline composition could also be employed in a rupturable container such as those used in diffusion transfer processes. In that case, the composition is applied to the element by passing it and a spreader sheet through pressure-applying members to rupture the container and spread the composition therebetween. In general, the processing composition employed in my system contains the developing agent for development, although the composition could also just be an alkaline solution when the developer is incorporated in the photosensitive element, in which case the alkaline solution serves to activate the incorporated developer.

In the formula listed above for the compounds which are alkali-cleavable upon oxidation, R is preferably hydrogen, although it could be any hydrolyzable entity well-known to those skilled in the art, e.g., acetyl, mono-, di- or trichloroacetyl radicals, perfluoroacyl, pyruvyl, alkoxyacyl, nitrobenzoyl, cyanbenzoyl, sulfonyl, sulfinyl, etc.

The nature of the ballast group in the formula for the compounds described above (Ballast) is not critical as long as it confers nondiffusibility to the compounds. Typical ballast groups include long-chain alkyl radicals linked directly or indirectly to the compound as well as aromatic radicals of the benzene and naphthalene series indirectly attached or fused directly to the benzene nucleus, etc. Useful ballast groups generally have at least 8 carbon atoms such as a substituted or unsubstituted alkyl group of 8 to 22 carbon atoms, an amide radical having 8 to 30 carbon atoms, a keto radical having 8 – 30 carbon atoms, etc., and may even comprise a polymer backbone or a dye or dye precursor (Z) as defined below, e.g.,





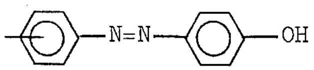
, etc.,

wherein G, R$_1$ and Z have the same definitions as in the formula above.

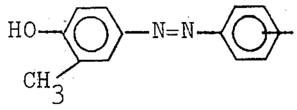
In addition to Ballast, the benzene nucleus in the above formula may have groups or atoms attached thereto such as the halogens, alkyl, aryl, alkoxy, aryloxy, nitro, amine, alkylamino, arylamino, amido, cyano, alkylmercapto, keto, carboalkoxy, heterocyclic groups, etc. In addition, such groups may combine together with the carbon atoms to which they are attached on the ring to form another ring which may be saturated or unsaturated including a carbocyclic ring, a heterocyclic ring, etc. Preferably an aromatic ring is directly fused to the benzene nucleus which would form, for example, a naphthol. Such a p-sulfonamidonaphthol is considered to be a species of a p-sulfonamidophenol and thus included within the definition. The same is true for p-sulfonamidoanilines employed in the invention.

As previously mentioned, Z in the above formula represents a bleachable dye haaving a predominant spectral absorption within the region of the visible spectrum to which the associated silver halide emulsion is sensitive, or a dye precursor. Such bleachable dyes are preferably azo dyes although other bleachable dyes, such as formazan dyes described in U.S. Pat. No. 3,503,741, would also be useful. Dye precursors can also be employed in my invention so long as they provide a bleachable dye at some stage of the process, preferably during development. Dye precursor moieties which could be used include leuco dyes, "shifted" dyes which shift hypsochromically or bathochromically when subjected to a different environment such as a change in pH, reaction with a material to form a complex, etc. These compounds may contain a solubilizing group if desired. Examples of such dye groups include the following:

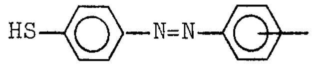
4-Hydroxy azobenzene

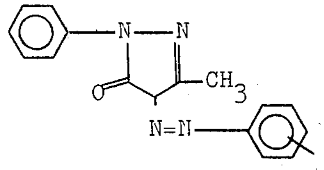


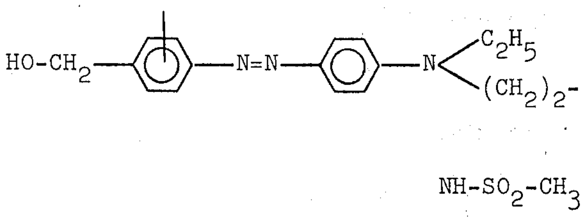
3-methyl-4-hydroxy azobenzene

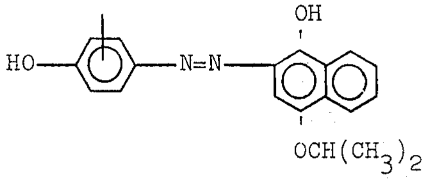


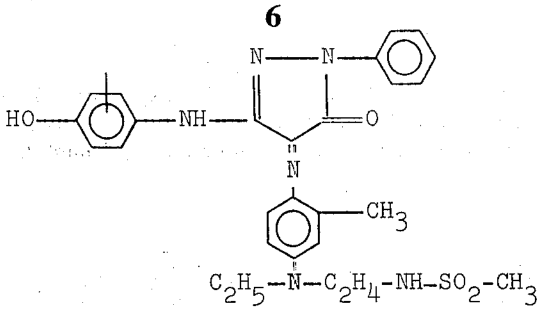
p-sulfhydryl azobenzene









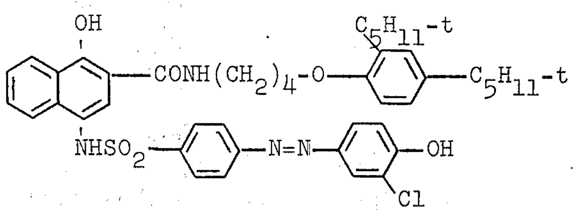


When dye precursor moieties are employed in my invention instead of dyes, they are converted to dyes by means well-known to those skilled in the art, e.g., oxidation, either in the photosensitive element, in the processing composition or at some stage in the process to form a visible dye. Such techniques are disclosed, for example, in British Pat. Nos. 1,157,501; 1,157,502; 1,157,503; 1,157,504; 1,157,505; 1,157,506; 1,157,507; 1,157,508; 1,157,509; 1,157,510 and U.S. Pat. Nos. 2,774,668; 2,698,798; 2,698,244; 2,661,293; 2,559,643; etc.

Expecially preferred compounds which can be employed in the process of my invention include the following:

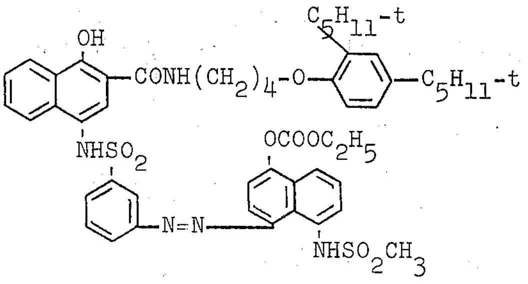
Compound No. 1

4-[4-(3-chloro-4-hydroxyphenylazo)benzenesulfonamido]-N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-2-naphthamide



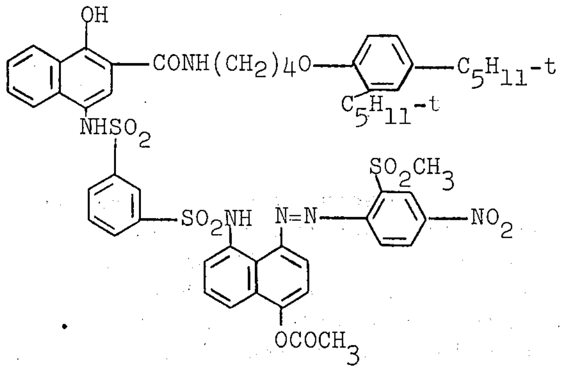
Compound No. 2

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[4-ethoxycarbonyloxy-8-methanesulfonamido-1-naphthylazo]benzenesulfonamido}-2-naphthamide



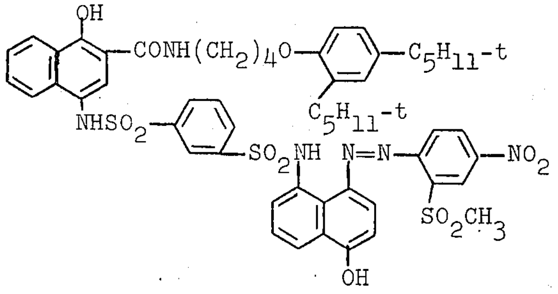
Compound No. 3

1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)-butyl]-4-{3-[5-acetoxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthylsulfamoyl]benzenesulfonamido}-2-naphthamide.



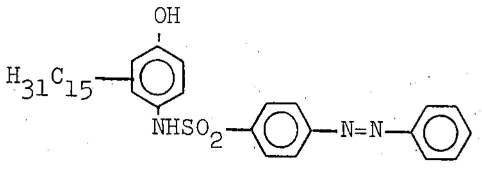
Compound No. 4

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[5-hydroxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthylsulfamoyl]benzenesulfonamido}-2-naphthamide.



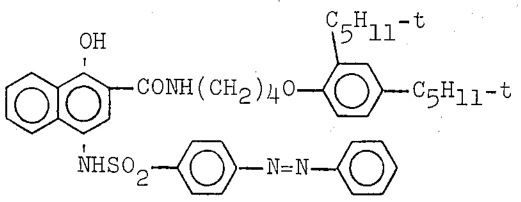
Compound No. 5

3-Pentadecyl-4-(p-phenylazobenzenesulfonamido)-phenol



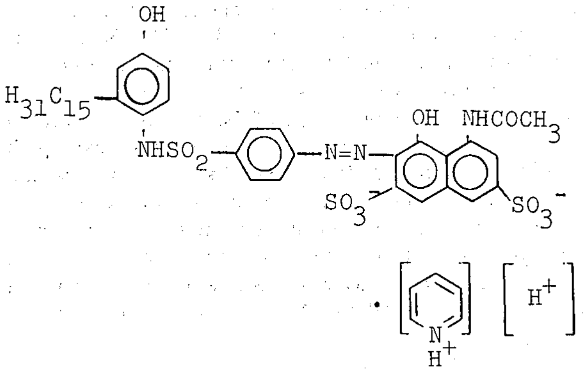
Compound No. 6

1-Hydroxy-4-(p-phenylazobenzenesulfonamido)-2[δ-(2,4-di-tert-amylphenoxy)-n-butyl]-naphthamide



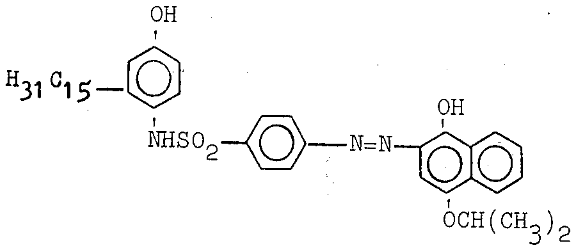
Compound No. 7

8-Acetamido-3,6-disulfo-2-{p-[(4-hydroxy-2-pentadecyl)phenylsulfamoyl]-phenylazo}-1-naphthol monopyridinium salt



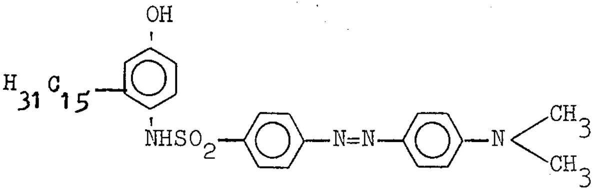
Compound No. 8

2-{p-[(4-Hydroxy-2-pentadecyl)phenylsulfamoyl]-phenylazo}-4-isopropoxynaphthol



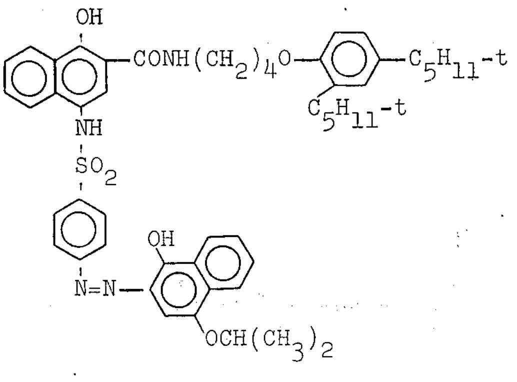
Compound No. 9

4-{p-[4'-(N,N-Dimethylamino)-phenylazo]-benzenesulfonamido}-3-pentadecylphenol



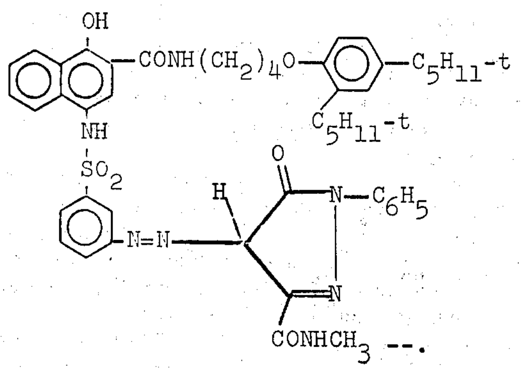
Compound No. 10

1-Hydroxy-4-[4-(1-hydroxy-4-isopropoxy-2-naphthylazo)-benzenesulfonamido]-2-[δ-(2,4-di-tertamylphenoxy)-n-butyl]-naphthamide



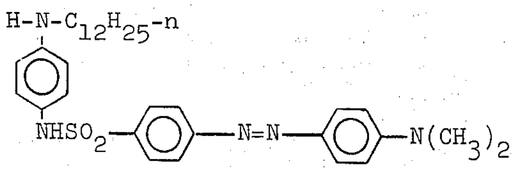
Compound No. 11

1-Hydroxy-4-[3-(1-phenyl-3-methylcarbamyl4-pyrazolin-5-onylazo)-benzenesulfonamido]-2-[δ-(2,4-di-tertamylphenoxy)-n-butyl]-naphthamide



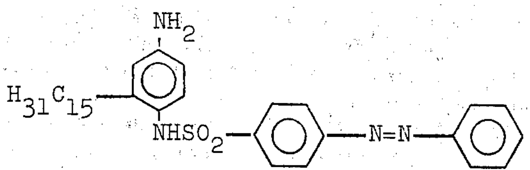
Compound No. 12

4-[p-(4'-Dimethylaminophenylazo)-benzenesulfonamido]-N-n-dodecylaniline



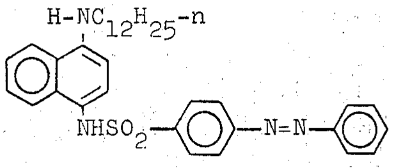
Compound No. 13

3-Pentadecyl-4-(p-phenylazobenzenesulfonamido)-aniline



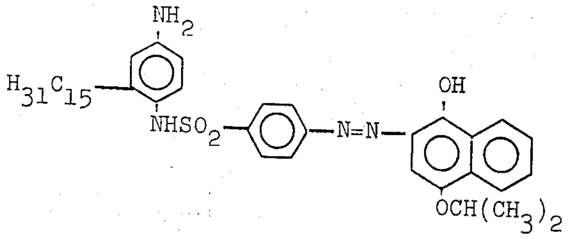
Compound No. 14

1-(N-n-Dodecylamino)-4-(p-phenylazobenzenesulfonamido)-naphthalene



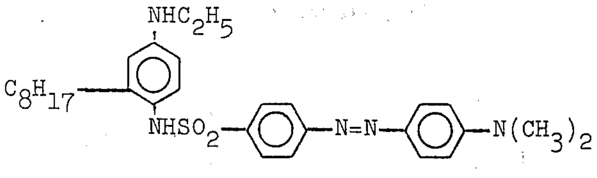
Compound No. 15

2-{p-[(4-amino-2-pentadecyl)-benzenesulfamyl]-phenylazo}-4-isopropoxynaphthol



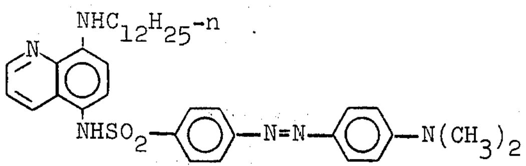
Compound No. 16

4-{p-[4'-(N',N'-dimethylamino)-phenylazo]-benzenesulfonamido}-3-octyl-N-ethylaniline



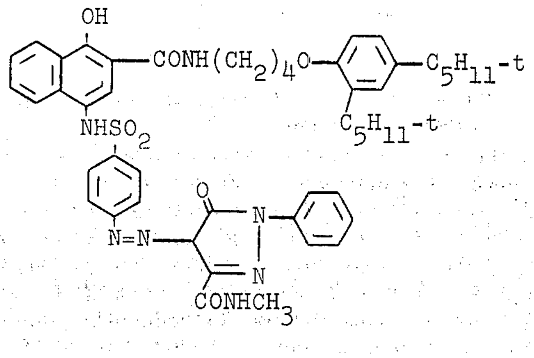
Compound No. 17

5-{p-[4'-(N,N-Dimethylamino)-phenylazo]-benzenesulfonamido}-8-(N'-n-dodecylamino)-quinoline



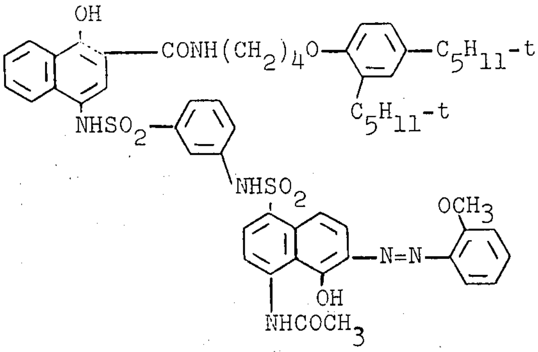
Compound No. 18

Yellow Dye-Releasing



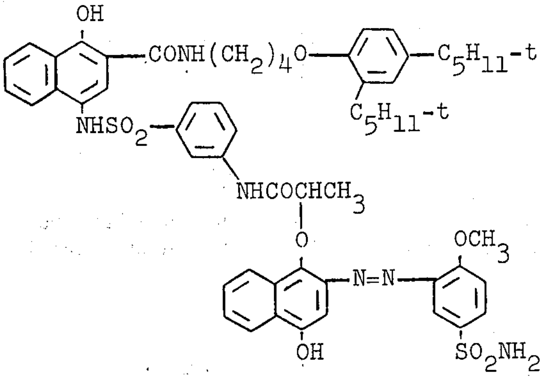
Compound No. 19

Magenta Dye-Releasing



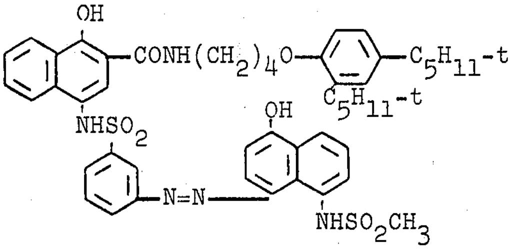
Compound No. 20

Magenta Dye-Releasing



Compound No. 21

Magenta Dye-Releasing



Of the above compounds, especially good results are obtained with Compound Nos. 1–4.

The process of the present invention may be used to produce positive images in single- or multicolors. In a three-color system, each silver halide emulsion layer of the photo-sensitive element will have associated therewith in an especially preferred embodiment of my invention a sulfonamido compound wherein the dye possesses a predominant spectral absorption within the region of the visible spectrum to which said silver halide emulsion is sensitive, i.e., the blue-sensitive silver halide emulsion layer will have a yellow sulfonamido compound associated therewith, the green-sensitive silver halide emulsion layer will have a magenta sulfonamido compound associated therewith, and the red-sensitive silver halide emulsion layer will have a cyan sulfonamido compound associated therewith. The sulfonamido compound associated with each silver halide emulsion layer may be contained either in the silver halide emulsion layer itself or in a layer contiguous the silver halide emulsion layer.

The concentration of the sulfonamido compounds, which are alkali-cleavable upon oxidation, employed in a preferred process of the present invention may be varied over a wide range depending upon the particular compound employed and the results which are desired. For example, the sulfonamido compounds employed in the present invention may be coated in layers by using coating solutions containing between about 0.5 and about 8 percent by weight of the sulfonamido compound distributed in a hydrophilic film-forming natural material or synthetic polymer, such as gelatin, polyvinyl alcohol, etc., which is adapted to be permeated by an aqueous alkaline processing composition.

Any silver halide developing agent can be employed in the process of my invention as long as it cross-oxidizes with the redox dye releaser compounds described herein. The developer may be employed in the photosensitive element to be activated by the alkaline processing composition. Specific examples of developers which can be employed in my invention include:

hydroquinone
N-methylaminophenol
Phenidone (1-phenyl-3-pyrazolidone)
Dimezone (1-phenyl-4,4-dimethyl-3-pyrazolidone)
N,N,N',N'-tetramethyl-p-phenylenediamine aminophenols
N,N-diethyl p-phenylenediamine
3-methyl-N,N-diethyl-p-phenylenediamine
3-methoxoy-N-ethyl-N-ethoxy-p-phenylenediamine, etc.

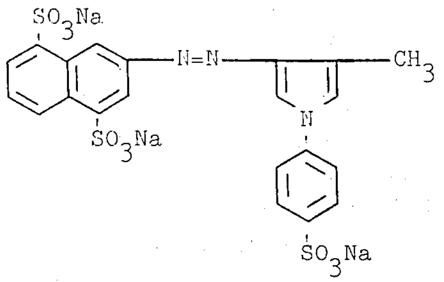
The black-and-white developers in this list are preferred, however, since they usually develop the emulsion faster.

The alkaline processing composition employed in the process of this invention is the conventional aqueous solution of an alkaline material, e.g., sodium hydroxide, sodium carbonate, an amine such as diethylamine, potassium hydroxide, etc.; preferably possessing a pH in excess of 12 and preferably containing a developing agent as described above. If desired, a thickener can be added to the processing composition to increase the viscosity of the composition and make it more adaptable for continuous processing. The viscous composition can then be removed by squeegeeing or water spraying.

The dye-bleach bath employed in the process of my invention is composed of any of the conventional materials heretofore used for such purpose. Reference is made, for example, to the materials disclosed in U.S. Pat. Nos. 3,414,411; 3,503,741; 3,498,787 and Canadian Pat. No. 790,533 referred to above. A catalyst is usually employed in such a bath such as a phenazine, a quinoxaline or an anthraquinone. Other catalysts are disclosed in U.S. Pat. Nos. 2,183,395 and 2,270,118. The catalyst may be incorporated in the emulsion, the alkaline processing composition, the dye-bleach bath, etc. These compounds bleach (i.e., oxidize) the metallic silver to silver ion and, in so doing, are reduced. The reduced catalyst then reduces the image dye. This redox reaction decolorizes the image dye and oxidizes the catalyst back to its original state.

The removal of metallic silver and silver halide from a photographic element is accomplished by employing a conventional bleach bath, fix bath, bleach-fix bath, etc. These materials are well known to those skilled in the art; e.g., Kodak F-5 Fix bath, ferric ethylenediamine tetraacetic acid and ammonium thiosulfate bleach-fix bath, etc. Other bleach baths are disclosed in U.S. Pat. Nos. 1,315,464; 1,946,640; 3,342,589; J. S. Mot. Pict. Eng., 17, 1931 (pp 1023–1027); and other bleach fix-baths are disclosed in German Pat. No. 866,605 and U.S. Pat. Nos. 2,748,000 and 3,706,561, the disclosures of which are hereby incorporated by reference.

It is also possible in accordance with my invention to combine the dye-bleach step with the bleach-fix step. This reduces the number of separate steps involved in processing and is quite advantageous. In such a case, a competing oxidant is employed such as Taylor yellow dye:



In accordance with the process of my invention, the film unit is exposed and the alkaline processing composition is applied to the fluid unit. The processing composition then permeates the various layers to initiate development of the exposed photosensitive silver halide emulsion layers. The developing agent develops each of the silver halide emulsion layers in the exposed areas, reducing silver halide to silver metal, and causing the developing agent to become oxidized imagewise. The oxidized developing agent then cross-oxidizes the redox dye releaser compounds, the oxidized form of which undergoes a base-catalyzed reaction to release the preformed dyes or the dye precursors imagewise as a function of the imagewise exposure of each of the silver halide emulsion layers. At least a portion of the imagewise distributions of diffusible dyes or dye precursors diffuses out of the photographic element. The diffusible moiety is transferable in the alkaline processing composition either by virtue of its self-diffusivity or by having attached to it one or more solubilizing groups such as COOH, SO_3H, OH, SH, etc.

The process of my invention is readily adaptable to a diffusion transfer format and such is considered to be within the scope of my invention. In such an application, the various materials employed in the processing steps described herein can be employed in rupturable containers or incorporated in the photosensitive element or spreader sheet. The various process steps of my invention may thus be combined or performed in a different order that set out above. In such a format, the diffusible dye which diffuses out of the element would be deposited on an image-receiving sheet which may or may not be the same as the spreader sheet mentioned above. This image-receiving sheet would then be peeled apart from the reset of the film unit so that the positive dye image in the photographic element may be viewed.

The various silver halide emulsion layers of a color film assembly employed in the process of the invention can be disposed in the usual order, i.e., the blue-sensitive silver halide emulsion layer first with respect to the exposure side, followed by the green-sensitive and red-sensitive silver halide emulsion layers. If desired, a yellow dye layer or a Carey Lea silver layer can be present between the blue-sensitive and green-sensitive silver halide emulsion layer for absorbing or filtering blue radiation that may be transmitted through the blue-sensitive layer. If desired, the selectively sensitized silver halide emulsion layers can be disposed in a different order, e.g., the blue-sensitive layer first with respect to the exposure side, followed by the red-sensitive and green-sensitive layers.

The silver halide emulsions used in this invention are the conventional, negative-working silver halide emulsions and comprise, for example, silver chloride, silver bromide, silver chlorobromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions can be coarse- or fine-grain and can be prepared by any of the well-known procedures, e.g., single-jet emulsions such as those described in Trivelli and Smith. *The Photographic Journal*, Vol. LXXIX, May 1939 (pp 330–338), doublejet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al U.S. Pat. No. 2,222,264 issued Nov. 19, 1940; Illingsworth U.S. Pat. No. 3,320,069 issued May 16, 1967; and McBride U.S. Pat. No. 3,271,157 issued Sept. 6, 1966. The emulsions may be regular-grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, Vol 12, No. 5, Sept./Oct., 1964 (pp 242–251).

The supports for the photographic elements employed in the process of this invention can be any material as long as it does not deleteriously effect the photographic properties of the film unit and is dimensionally stable. For positive transparencies and cine film, transparent supports are preferred such as cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethyleneterephthalate) film, polycarbonate film, poly-α-olefins such as polyethylene and polypropylene film, and related films or resinous materials. The support is usually about 2 to 6 mils in thickness.

The silver halide emulsions useful in the process of my invention are well-known to those skilled in the art and are described in *Product Licensing Index*, Vol. 92, December, 1971, publication 9232, p. 107, paragraph I, "Emulsion types"; they may be chemically and spectrally sensitized as described on p. 107, paragraph III, "Chemical sensitization," and pp. 108–109, paragraph XV, "Spectral sensitization," of the above article; they can be protected against the production of fog and can be stabilized against loss of sensitivity during keeping by employing the materials described on p. 107, paragraph V, "Antifoggants and stabilizers," of the above article; they can contain development modifiers, hardeners, and coating aids as described on pp. 107–108, paragraph IV, "Development modifiers"; paragraph

VII, "Hardeners"; and paragraph XII, "Coating aids," of the above article; they and other layers in the photographic elements used in this invention can contain plasticizers, vehicles and filter dyes described on p. 108, paragraph XI, "Plasticizers and lubricants," and paragraph VIII, "Vehicles," and p. 109, paragraph XVI, "Absorbing and filter dyes," of the above article; they and other layers in the photographic elements used in this invention may contain addenda which are incorporated by using the procedures described on p. 109, paragraph XVII, "Methods of addition," of the above article; and they can be coated by using the various techniques described on p. 109, paragraph XVIII, "Coating procedures," of the above article, the disclosures of which are hereby incorporated by reference.

The following examples illustrate the process of the invention.

EXAMPLE I

A multilayer, multicolor photographic element is prepared by coating the following layers in the order recited on a transparent cellulose acetate film support:

1. red-sensitive, negative-working, gelatin-silver bromide emulsion (200 mg gelatin/ft^2 and 100 mg silver/ft^2) and compound 4 (140 mg/ft^2 which is 1.3×10^{-4} M);
2. interlayer of gelatin (100 mg/ft^2), developing agent 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone (10 mg/ft^2) and 2,5-di-sec-dodecylhydroquinone (100 mg/ft^2);
3. green-sensitive, negative-working, gelatin-silver bromide emulsion (200 mg gelatin/ft^2 and 100 mg silver/ft^2), compound 2 (125 mg/ft^2 which is 1.3×10^{-4} M) and diethyl lauramide (125 mg/ft^2);
4. interlayer of gelatin (100 mg/ft^2), developing agent 4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone (10 mg/ft^2), 2,5-di-sec-dodecylhydroquinone (100 mg/ft^2) and Carey Lea Silver 10 mg/ft^2);
5. blue-sensitive, negative-working, gelatin-silver bromide emulsion (200 mg gelatin/ft^2 and 100 mg silver/ft^2), compound 1 (102 mg/ft^2 which is 1.3×10^{-4} M) and diethyl lauramide (102 mg/ft^2); and
6. overcoat of gelatin (80 mg/ft^2).

Samples of the above prepared element are exposed on an Eastman 1b (Trademark) sensitometer using an exposure chart which allows additive red, green and blue exposures to achieve complete color separation. The exposure conditions are: a) red light for one second, b) blue light for 1/10 second, and c) green light for 1/10 second. One sample of the exposed element is then processed as follows:

1. Development - one min. at 37.8°C by employing the following activator:

NaOH	20	g
KBr	10	g
Phenylmercaptotetrazole	0.03	g
Water to one liter		

2. Fix - one min at 22.2°C with Kodak F-5 Fix bath:

Sodium thiosulfate	240	g
Sodium sulfite	15	g
Acetic acid (28%)	48	ml
Boric acid (crystals)	7.5	g
Potassium aluminum sulfate	15	g
Water to one liter		

3. Dye-Bleach - 30 sec. at 37.8°C with:

12.1 N HCl	100	ml
Thiourea	100	g
Phenazine	0.2	g
Water to one liter		

4. Bleach-Fix - one min. at 37.8°C with a conventional ferric ethylenediamine tetracetic acid and ammonium thiosulfate bleach-fix bath
5. Stabilizer Rinse - ten sec. at 22.2°C with: Na_2CO_3 50 g/l Cetyl trimethylammonium bromide 5.0 g/l
6. Dry.

A second sample of the exposed element is processed in the same manner except that the Dye Bleach bath (step 3) is omitted. The following sensitometric results are obtained:

	DENSITIES					
	With Dye-Bleach Bath			Without Dye-Bleach Bath		
Exposure	Red	Green	Blue	Red	Green	Blue
Cyan	3.34	0.65	0.88	4.12	1.10	1.32
Magenta	0.36	1.51	1.09	1.48	2.31	1.62
Yellow	0.18	0.47	2.09	1.27	0.85	2.25
Red	0.27	2.28	2.68	1.11	2.72	3.04
Green	3.33	0.98	2.32	3.98	1.24	2.51
Blue	3.36	2.24	1.27	4.05	2.68	1.72
Neutral D_{min}	0.25	0.28	0.75	1.57	0.82	1.39
D_{max}	3.43	3.23	3.07	4.00	3.20	3.07

The above results reveal a significant improvement in D_{min} without adversely effecting D_{max} when the dye-bleach bath is employed.

EXAMPLE II

A second multilayer, multicolor, photographic element is prepared similar to Example I except that compound 4 is replaced with compound 3 at equimolar amount in layer 1. The element is exposed and processed as in Example I except that the Dye-Bleach treatment of step 3 is for two minutes. The following sensitometric results are obtained:

	DENSITIES					
	With Dye-Bleach Bath			Without Dye-Bleach Bath		
Exposure	Red	Green	Blue	Red	Green	Blue
Cyan	3.69	1.14	1.08	3.74	1.51	1.34
Magenta	0.41	1.70	1.17	1.65	2.23	1.73
Yellow	0.25	0.48	2.34	1.49	1.09	2.59
Red	0.36	2.67	3.11	1.26	2.81	3.25
Green	3.60	1.46	2.81	3.60	1.70	2.80
Blue	3.60	2.56	1.36	3.68	2.78	1.69
Neutral D_{min}	0.31	0.36	0.84	1.80	1.18	1.48
D_{max}	3.65	3.50	3.36	3.68	3.60	3.51

As in Example I, the above results reveal a significant improvement in D_{min} without adversely affecting D_{max} when the Dye-Bleach bath is employed.

EXAMPLE III

Combined Dye-Bleach and Bleach-Fix Stops

A multilayer, multicolor, photographic element is prepared similar to Example I. The element is exposed as in Example I and processed as follows:

1. Development - same as in Example I.
2. Dye-Bleach and Bleach-Fix - one min at 37.8°C by employing the following solution:

Hydrochloric acid (12.1 N)	100	ml
Thiourea	100	g
Phenazine	0.25	g
Taylor yellow dye (see formula above)	3.0	g
Water to 1 liter		

3. Stabilizer Rinse - same as in Example I.

Well-defined positive images having improved minimum densities similar to the results of Example I were obtained in the processed photographic element.

The invention has been described with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

I claim:

1. A process for producing a color image comprising:

I. imagewise exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, said emulsion layer having associated therewith a nondiffusible redox dye releaser which will redox with oxidized developing agent to release a diffusible, bleachable dye, said redox dye releaser being a ballasted, bleachable dye wherein the ballast group is linked to the dye through a linkage which is cleavable upon oxidation;

II. treating said photosensitive element with an alkaline processing composition in the presence of a silver halide developing agent to effect development of each of said exposed silver halide emulsion layers, thereby oxidizing said developing agent and forming a metallic silver image;

a. said oxidized developing agent thereby crossoxidizing said redox dye releaser;

b. said oxidized redox dye releaser then cleaving, thus forming an imagewise distribution of diffusible, bleachable dye which diffuses out of said element;

III. bleaching said element to decolorize any imagewisereleased dye which has not diffused out of said element; and

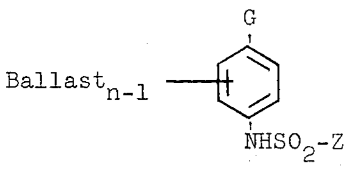
IV. removing said metallic silver and silver halide from said element by bleaching and fixing;

whereby a dye image is obtained in said element which is the reverse of said metallic silver image.

2. The process of claim **1** wherein said silver halide emulsion is negative-working.

3. The process of claim **1** wherein said support is transparent.

4. The process of claim **1** wherein said redox dye releaser is a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible dye from the benzene nucleus and having the formula:



wherein:

a. Z is a bleachable dye having a predominant spectral absorption within the region of the visible spectrum to which said associated silver halide emulsion is sensitive or a dye precursor;

b. Ballast is an organic ballasting radical of such molecular size and configuration as to render the sulfonamido compound nondiffusible during development in an alkaline processing composition;

c. G is OR or NHR$_1$ wherein R is hydrogen or a hydrolyzable moiety and R$_1$ is hydrogen or an alkyl group of 1 to 22 carbon atoms; and

d. n is a positive integer of 1 to 2 and is 2 when G is OR or when R$_1$ is hydrogen or an alkyl group of less than 8 carbon atoms.

5. The process of claim **4** wherein Z is an azo dye.

6. The process of claim **4** wherein G is OH or NH$_2$.

7. The process of claim **4** wherein an aromatic ring is directly fused to said benzene nucleus to provide a sulfonamidonaphthol compound.

8. The process of claim **4** wherein said photosensitive element comprises a support having thereon red-, green- and bluesensitive silver halide emulsion layers having associated therewith a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible cyan, magenta and yellow dye, respectively, from the benzene nucleus, said dyes being azo dyes.

9. The process of claim **8** wherein said support is transparent and each of said silver halide emulsions is negativeworking, whereby a positive transparency is obtained.

10. The process of claim **4** wherein said sulfonamido compound is:

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[5-hydroxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthylsulfamoyl]benzenesulfonamido}-2-naphthamide;

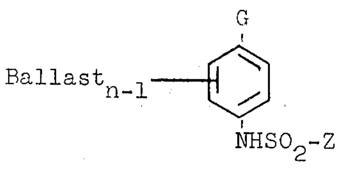
1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-{3-[5-acetoxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthylsulfamoyl]benzenesulfonamido}-2-naphthamide;

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[4-ethoxycarbonyloxy-8-methanesulfonamido-1-naphthylazo]benzenesulfonamido}-2-naphthamide; or

4-[4-(3-chloro-4-hydroxyphenylazo)benzenesulfonamido]-N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-2-naphthamide.

11. A process for producing a color image comprising:

I. imagewise exposing a photosensitive element comprising a support having thereon at least one photosensitive silver halide emulsion layer, said emulsion layer having associated therewith a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible, bleachable dye from the benzene nucleus and having the formula:



wherein:

a. Z is a bleachable dye having a predominant spectral absorption within the region of the visible spectrum to which said associated silver halide emulsion is sensitive or a dye precursor;

b. Ballast is an organic ballasting radical of such molecular size and configuration as to render the sulfonamido compound nondiffusible during development in an alkaline processing composition;

c. G is OR or NHR_1 wherein R is hydrogen or a hydrolyzable moiety and R_1 is hydrogen or an alkyl group of 1 to 22 carbon atoms; and

d. n is a positive integer of 1 to 2 and is 2 when G is OR or when R_1 is hydrogen or an alkyl group of less than 8 carbon atoms;

II. treating said photosensitive element with an alkaline processing composition in the presence of a silver halide developing agent to: (1) cause any dye precursor present to become a dye having a predominant spectral absorption within the region of the visible spectrum to which said associated silver halide emulsion is sensitive, said dye being bleachable; and (2) to effect development of each of said exposed silver halide emulsion layers, thereby oxidizing said developing agent and forming a metallic silver image;

a. said oxidized developing agent thereby cross-oxidizing said sulfonamido compound; and

b. said oxidized sulfonamido compound then cleaving, thus forming an imagewise distribution of diffusible, bleachable dye which diffuses out of said element;

III. bleaching said element to decolorize any imagewise-released dye which has not diffused out of said element; and

IV. removing said metallic silver and silver halide from said element by bleaching and fixing,

whereby a dye image is obtained in said element which is the reverse of said metallic silver image.

12. The process of claim **11** wherein Z is an azo dye.

13. The process of claim **11** wherein G is OH or NH_2.

14. The process of claim **11** wherein an aromatic ring is directly fused to said benzene nucleus to provide a sulfonamidonaphthol compound.

15. The process of claim **14** wherein Z is an azo dye.

16. The process of claim **11** wherein said photosensitive element comprises a support having thereon red-, green- and blue-sensitive silver halide emulsion layers having associated therewith a nondiffusible p-sulfonamidoaniline or p-sulfonamidophenol which is alkali-cleavable upon oxidation to release a diffusible cyan, magenta and yellow dye, respectively, from the benzene nucleus, said dyes being azo dyes.

17. The process of claim **11** wherein said silver halide emulsion is negative-working.

18. The process of claim **11** wherein said support is transparent.

19. The process of claim **16** wherein said support is transparent and each of said silver halide emulsions is negativeworking, whereby a positive transparency is obtained.

20. The process of claim **19** wherein said sulfonamido compound is:

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[5-hydroxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthysulfamoyl]benzenesulfonamido}-2-naphthamide;

1-hydroxy-N-[4-(2,4-di-t-pentylphenoxy)butyl]-4-{3-[5-acetoxy-6-(2-methylsulfonyl-4-nitrophenylazo)-1-naphthylsulfamoyl]benzenesulfonamido}-2-naphthamide;

N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-4-{3-[4-ethoxycarbonyloxy-8-methanesulfonamido-1-naphthylazo]benzenesulfonamido}-2-naphthamide; or

4-[4-(3-chloro-4-hydroxyphenylazo)benzenesulfonamido]-N-[4-(2,4-di-t-pentylphenoxy)butyl]-1-hydroxy-2-naphthamide.

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