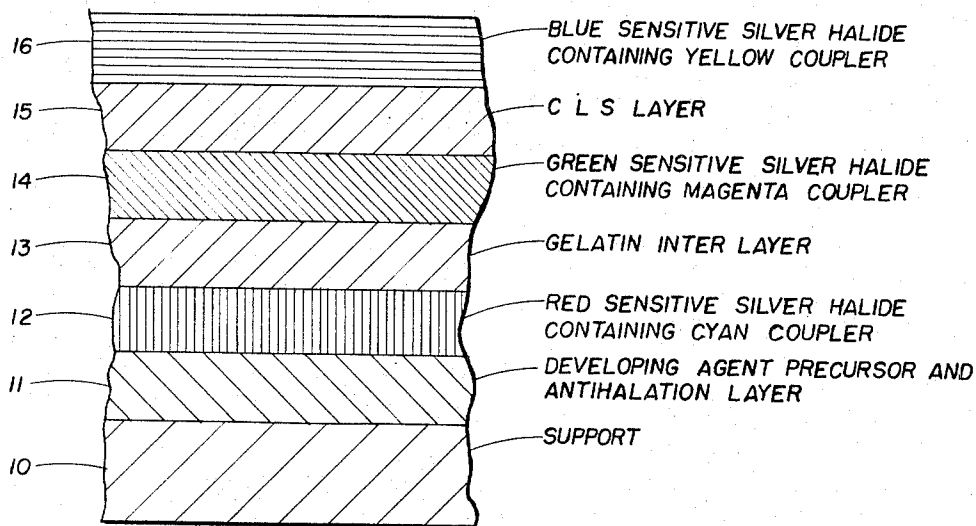


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D. P. HARNISH ETAL
COLOR DEVELOPER PRECURSOR

3,342,597

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DONALD P. HARNISH
RICHARD L. REEVES
INVENTORS

BY *R. Frank Smith*
Henry E. Byers
ATTORNEYS

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3,342,597

COLOR DEVELOPER PRECURSOR

Donald P. Harnish and Richard L. Reeves, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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This invention concerns compounds releasing developing agents upon treatment with aqueous alkaline activator solutions, more particularly developing agent precursors which release p-phenylenediamines in an alkaline solution.

In the preparation of silver halide emulsions for recording colors, it is customary to incorporate a color forming material in the silver halide emulsion so that upon color development this color forming compound (coupler) reacts with the oxidation product of the developing agent to form a dye. In the typical emulsion for recording the visible spectrum, the emulsion is coated in several layers, each sensitive to a particular region of the spectrum. By suitable control of the development and by use of several couplers, it is possible to form the proper dye in each layer to give an adequate color representation of the light image producing the original exposure.

The developing agent which is most customarily used with color emulsions is a p-phenylenediamine. The p-phenylenediamine is used in a developing bath since it has not been feasible to incorporate this developer in the silver halide emulsion. An emulsion having a p-phenylenediamine incorporated therein is unstable due to reaction of the developer with the light sensitive silver halide. Accordingly, it has been desirable to find a means of incorporating a p-phenylenediamine developer or precursor thereof in a silver halide emulsion and, at the same time, to provide a stable silver halide emulsion.

We have found that certain indoaniline dyes can be incorporated into a silver halide emulsion without having any deleterious effect on the emulsion. The indoaniline dye releases a p-phenylenediamine developer when the coating is activated by immersion in an alkaline activator solution having a pH of about 11. However, pH values as low as 9 and as high as 14 may be used. Superior results are obtained in a preferred range of 11–13.5. The p-phenylenediamine developer thus released develops the silver halide to silver in the usual manner. The oxidized form of the p-phenylenediamine reacts with color couplers to form the desired dyes in the emulsion.

Bleaching and attendant steps normally used in processing color photographic elements can then be carried out. The alkaline medium may be a liquid bath or may be in vapor form, such as ammonia vapors or other alkaline vapors, depending on the developing agent precursor used.

One object of this invention is to provide a silver halide emulsion containing a developing agent precursor which releases a p-phenylenediamine in an alkaline bath. An additional object is to provide a color emulsion containing at least one color coupler which reacts with oxidized p-phenylenediamine to form a dye and which contains a developing agent precursor (i.e. a dye) which cleaves under alkaline conditions to give a p-phenylenediamine. Another object is to provide photographic color materials which can be processed by alkaline solutions or by alkaline vapor. A further object is to provide a

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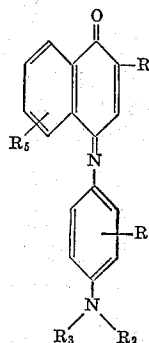
method of incorporating different developing agent precursors in different layers of a multilayer color film.

The amount of developing agent precursor required for incorporation into a photographic coating is dependent upon the particular requirements of the coating structure and can vary from a fraction to several moles of developing agent precursor per mole of silver halide in said coating. However, a particularly useful range of concentrations of developing agent precursor, according to our invention, is from 1–3 moles of developing agent precursor for every mole of image dye formed.

The developing agent precursors of this invention may be incorporated into the emulsion layers or gelatin interlayers of a photographic coating by different methods. A typical procedure for accomplishing finely divided particulate dispersions and avoiding unwanted crystallization or other aggregation of particles is the "Fischer" method in which an organic compound is provided with a solubilizing group such as, for example, a sulfonic acid group, so that it can be dissolved in water as the alkali metal salt, and the resultant solution added to the aqueous gelatin coating composition. This "Fischer" technique as applied to dye-forming couplers is described, for example, in U.S. Patent 2,186,849, issued Jan. 9, 1940. Such a method is convenient for incorporating those developing agent precursors of the present invention which contain at least one of the above mentioned solubilizing groups.

Another typical method for incorporating compounds in finely divided, noncrystallized form is the solvent-dispersion technique in which the organic compound is dissolved in an organic solvent and the resulting solution is intimately blended in an aqueous gelatin solution. This technique, as applied to couplers, is described, for example, in U.S. Patents 2,322,027, issued June 15, 1943; 2,801,170 and 2,801,171, both issued July 30, 1957; 2,870,012, issued Jan. 20, 1959, and 2,991,177, issued July 4, 1961. This solvent dispersion technique can be used to incorporate into aqueous gelatin coating compositions those developing agent precursors of the present invention which contain no solubilizing groups.

Compounds useful as developing agent precursors according to our invention correspond to the following general formula:



where:

R=electron withdrawing groups such as $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$, $-\text{CONHR}_4$, (R_4 =hydrogen, alkyl of one

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to four carbon atoms, substituted alkyl of one to four carbon atoms, e.g. $-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$,

$-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$

$-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, etc., phenyl, substituted phenyl,

e.g. $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$

$-\text{C}_6\text{H}_3(\text{COOH})_2$, etc.).

R_2 =hydrogen, alkyl of one to four carbon atoms or substituted alkyl as in R_4 above, and alkoxy, e.g. methoxy, substituted alkoxy, similar to substituted alkyl in R_4 above.

R_2 =alkyl and substituted alkyl as in R_4 above.

R_3 =alkyl and substituted alkyl as in R_4 above.

R_5 =hydrogen and solubilizing groups, e.g. $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{SO}_2\text{NHCH}_3$, $-\text{SO}_2\text{NH}_2$, $-\text{NHSO}_2\text{CH}_3$, etc.

R_1 , R_2 , R_3 , R_4 , and R_5 may be alike or different, and the total number of carbon atoms comprising R_1 , R_2 , R_3 , R_4 and R_5 preferably does not exceed 15.

These development precursors are indoaniline dyes which are decomposed when exposed to an activator solution having a pH of at least 9 and preferably from 11-13.5. When the developing agent precursors of our invention are dispersed directly into the gelatin coatings, the gelatin functions as a protective colloid thus preventing the precipitation or micelle formation of said compound to take place. The developing agent precursors of our invention, which are dispersed in an organic solvent, such as diamylphenol, are kept in solution by the solvent. The alkaline activator solution attacks the developing agent precursor dissolved in the solvent causing it to cleave.

The moiety of the indoaniline dye which cleaves from the p-phenylenediamine moiety of the indoaniline dye will not couple with p-phenylenediamine. Therefore, the p-phenylenediamine is free to form a dye with the color forming coupler in the emulsion. The non-diffusible image-forming couplers useful in our invention couple with the oxidized form of paraphenylenediamine color developers to form stable dyes at the pH of the activator solution, i.e. from 9-14.

The p-phenylenediamine moiety has little effect on the rate of alkaline cleavage. Therefore, the choice of the p-phenylenediamine thus can be made on the basis of desired mobility, the developability of the silver halide, coupling reactivity, resulting color, etc. Any of the p-phenylenediamine developers known in the art may be used. Some specific types are disclosed in the Journal American Chemical Society, 73, 3100 (1951), R. L. Bent et al.

Typical cyan, magenta, and yellow forming couplers useful in this invention to form non-diffusible dyes on coupling with oxidation products of oxidized color developing agents may be found, for example, in the following U.S. patents.

Cyan:

2,895,826, Salminen et al., July 21, 1959
2,474,293, Weissberger et al., June 23, 1949
2,908,573, Bush et al., Oct. 13, 1959

Magenta:

2,600,788, Loria et al., June 17, 1952.
2,908,573, Bush et al., Oct. 13, 1959

Yellow:

2,875,057, McCrossen et al., Feb. 24, 1959
2,908,573, Bush et al., Oct. 13, 1959

The following are typical examples of the couplers which may be used.

Cyan dye forming couplers:

1-hydroxy-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-2-naphthamide

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1-hydroxy-N-[δ -(2,4-di-tert-amylphenoxy)butyl]-4-chloro-2-naphthamide

1-hydroxy-N-[β -(2,4-di-tert-amylphenoxy)ethyl]-2-naphthamide

1-hydroxy-N-[β -(2,4-di-tert-amylphenoxy)ethyl]-4-chloro-2-naphthamide

1-hydroxy-N-[δ -(2,4-di-tert-amylphenoxy)propyl]-2-naphthamide

1-hydroxy-N-[δ -(2-n-butyl-4-tert-amylphenoxy)butyl]-2-naphthamide

1-hydroxy-N-[δ -(p-tert-amylphenoxy)butyl]-2-naphthamide

1-hydroxy-N-[β -[α -(2,4-tert-diamylphenoxy)acetamido]ethyl]-2-naphthamide

1-hydroxy-N-[β -[α -(2,4-tert-diamylphenoxy)acetamido]ethyl]-4-chloro-2-naphthamide

1-hydroxy-N-[δ -[α -(2,4-tert-diamylphenoxy)acetamido]butyl]-2-naphthamide (U.S. 2,895,826, compounds 4, 5, 6)

5-[α -(2,4-di-n-amylphenoxy)acetamido]-2-heptafluorobutyramidophenol

5-[α -(2,4-di-tert-amylphenoxy)butyramido]-2-heptafluorobutyramidophenol

5-[α -(2,4-di-n-amylphenoxy)butyramido]-2-heptafluorobutyramidophenol

Magenta dye forming couplers:

1-(2,4-dichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

1-(2,5-dichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

1-(2,4,6-tribromophenyl)-3-[3-(2,4-di-tert-amylphenoxyacetamido)benzamido]-5-pyrazolone

1-(2,4,6-trichlorophenyl)-3-[β -(2,4-di-tert-amylphenoxy)propionamido]-5-pyrazolone

1-(2,4,6-tribromophenyl)-3-[3-(4-tert-amylphenoxy)benzamido]-5-pyrazolone

1-(2,5-dichlorophenyl)-3-[3-(4-tert-amylphenoxy)benzamido]-5-pyrazolone

1-(2,4,6-tribromophenyl)-3-[3-(4-tert-amylphenoxy)benzamido]-5-pyrazolone (U.S. 2,908,573, Compounds 6 and 7)

1-(2,4,6-trichlorophenyl)-3-[α -(3-pentadecylphenoxy)butyramido]-5-pyrazolone

1-(2,4,6-trichlorophenyl)-3-[3-[α -(3-pentadecylphenoxy)butyramido]-benzamido]-5-pyrazolone

Yellow dye forming couplers:

4-benzoylacetoamido-3-methoxy-(2,4-di-tert-amylphenoxy)acetanilide

α -Benzoyl-5-[α -(2,4-di-tert-amylphenoxy)butyramido]-2-methoxyacetanilide

3-benzoylacetoamino-4-methoxy-(2,4-di-tert-amylphenoxy)acetanilide

α -{3-[α -(2,4-di-tert-amylphenoxy)acetamido]benzoyl}-2-methoxyacetanilide

α -{4-[α -(2,4-di-tert-amylphenoxy)acetamido]benzoyl}-2-methoxyacetanilide

α -{3-[α -(2,4-di-tert-amylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide (U.S. 2,908,573, Compound 10)

α -{3-[α -(3-pentadecylphenoxy)butyramido]benzoyl}-2-methoxyacetanilide

Various color emulsions may be used and these emulsions may comprise various layer arrangements. For instance, the support may carry thereon a blue-sensitive layer containing a yellow coupler, an interlayer, a green-sensitive layer containing cyan and magenta couplers and having thereon an overcoat. These couplers may occur in different layers and in different orders as a matter of choice. It will be appreciated that various supports known

in the art may be used for the silver halide emulsion and that if the transparent support is used, that one or more light-sensitive layers may be coated on one side and one or more layers on the other side. Another useful photographic element may have a bleachable filter layer incorporated in the element between two light-sensitive layers or on the support when it is between the light-sensitive layers. In still another useful element, the light-sensitive elements can have one or more strata of the type described in Millikan U.S. Ser. No. 159,057, filed Dec. 13, 1961. For example, one stratum would be a high speed emulsion and the second stratum a low speed emulsion both optically sensitized to the same portion of the spectrum and producing the same dye image. Similarly, the second light-sensitive layer can have one or more stratum.

The photographic emulsion may contain a single coupler or a combination of couplers in one or more of the light-sensitive layers.

In the silver halide emulsions in the color element, various silver salts may be used as the sensitive salts, including silver bromide, silver iodide, silver chloride or silver halide such as silver chlorobromide, silver bromiodide, etc.

The emulsions can be chemically sensitized by any of the accepted procedures. The emulsions can be digested with naturally active gelatin, or sulfur compounds can be added such as those described in Sheppard U. S. Patent 1,574,944, issued Mar. 2, 1926; Sheppard et al. U.S. Patent 1,623,499, issued Apr. 5, 1927; and Sheppard et al. U.S. Patent 2,410,689, issued Nov. 5, 1946.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll U.S. Patent 2,487,850, issued Nov. 15, 1949), polyamines, such as diethyl triamine (Lowe and Jones U.S. Patent 2,518,698, issued Aug. 15, 1950), polyamines, such as spermine (Lowe and Allen U.S. Patent 2,521,925, issued Sept. 12, 1950), or bis(β -aminoethyl)sulfide and its water-soluble salts (Lowe and Jones U.S. Patent 2,521,926, issued Sept. 12, 1950).

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there may be employed as the carrier for the silver halide in its preparation, gelation or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound. Some colloids which may be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,326,808 of Lowe and Clark, issued Aug. 24, 1943, a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamine having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 on an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued Feb. 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued Aug. 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,154, issued Oct. 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued Oct. 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in U.S. Patent 2,852,382, of Illingsworth, Dann and Gates, issued Sept. 16, 1958.

Included among the green sensitizers are acid merocyanines of Brooker et al. U.S. Patent 2,493,747, issued Jan. 10, 1950, such as

3-(p-carboxyphenyl)-5-(3-methyl-2(3)-benzoxazolyli-dene)-rhodanine,

1-(p-carboxyphenyl)-4-[3-ethyl-2(3)-benzothiazolyli-deneisopropylidene]-3-methyl-5-pyrazolone,
3-ethyl-5-[(3-ethyl-2(3)-benzoxazolyli-dene)ethylidene]-2-[3-methyl-5-oxo-1-(p-sulphophenyl)-4-(2-pyrazolinyli-dene)]-4-thiazolidone, etc.;

the merocyanines of Brooker et al. U.S. Patent 2,493,748, issued Jan. 10, 1950, such as

3-carboxymethyl-5-[(3-methyl-2(3)-thiazolinyli-dene)-ethylidene]-2-thio-2,4(3,5)-oxazoledione,
5-[3-ethyl-2(3)-benzoxazolyli-dene)-ethylidene]-3-sulfo-methyl-2-thio-2,4(3,5)-oxazoledione, etc.;

the merocyanines of Sprague U.S. Patent 2,519,001, such as

5-[(3- β -carboxyethyl-2(3)-benzothiazolyli-dene)-ethylidene]-3-ethyl-1-phenyl-2-thiohydantoin, etc.;

the cyanine dyes of Sprague U.S. Patent 2,503,776, issued Apr. 11, 1950, such as

20 anhydro-5-chloro-1'-ethyl-3- β -sulfoethylthia-2'-cyanine hydroxide, etc.,

and other sensitizers well known in the art.

Included among the blue sensitizers are acid merocyanines of Brooker et al. U.S. 2,493,747, issued Jan. 10, 1950, such as

4-[(5-chloro-3-ethyl-2(3)-benzothiazolyli-dene)- α -ethyl-ethylidene]-3-methyl-1-(p-sulphophenyl)-5-pyrazolone, etc.;

30 the merocyanines of Brooker et al. U.S. Patent 2,493,748 such as

3-carboxymethyl-5-(3-ethyl-2(3)-benzothiazolyli-dene) rhodanine, etc.

35 and other sensitizers well known in the art.

A typical negative color process which can be used in our invention is described in detail by W. T. Hansen, Jr. and W. I. Kisner in an article in the "Journal of the Society of Motion Picture and Television Engineers," vol. 61 (1953), pages 667–701, incorporated herein by reference.

Example of U.S. Patent 2,944,900, also incorporated herein by reference, discloses a reversal color development process which can be used in our invention.

45 The attached drawing illustrates a multilayer color photographic element. A cellulose acetate opaque white film support has in order, beginning with the support, a gelatin layer 11 containing the developing agent precursor which also serves as the antihalation material.
50 Over the precursor layer is coated a gelatino-silver bromiodide emulsion 12 sensitized to red light, a gelatin interlayer 13, a gelatino-silver bromiodide emulsion layer 14 sensitized to green light, a yellow Carey Lea silver interlayer 15 containing colloidal silver particles,
55 and a gelatino-silver bromiodide emulsion 16 sensitized to blue light.

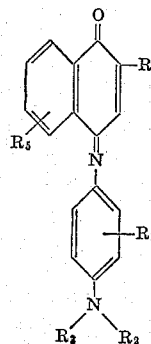
The following specific compounds serve to illustrate compounds useful in this invention, but do not limit same.

60 (1)

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Compound No.	R	R ₁	R ₂	R ₃	R ₄
1	—CONHCH ₂ CH ₂ SO ₃ Na	2-CH ₃	—CH ₂ CH ₂ NHSO ₃ CH ₃	—C ₂ H ₅	H
2	—CONHCH ₂ CH ₂ SO ₃ K	2-CH ₃	—CH ₂ CH ₂ SO ₃ K	—C ₂ H ₅	H
3	—CONHCH ₂ CH ₂ SO ₃ Na	H	—CH ₂ CH ₂ OH	—C ₂ H ₅	H
4		H	—CH ₂ CH ₂ OH	—C ₂ H ₅	H
5		H	—CH ₂ CH ₂ OH	—C ₂ H ₅	H
6	—COCH ₃	2-CH ₃	—CH ₂ CH ₂ SO ₃ Na	—C ₂ H ₅	H
7	—COCH ₃	H	—CH ₂ CH ₂ OH	—C ₂ H ₅	H
8	—COCH ₃	H	—C ₂ H ₅	—C ₂ H ₅	H
9	As in No. 1 above	As in No. 1	—C ₂ H ₅	—C ₂ H ₅	H
10	As in No. 1 above	2-OCH ₃	—C ₂ H ₅	—C ₂ H ₅	H
11	—CONH ₂	H	—C ₂ H ₅	—C ₂ H ₅	5-SO ₃ Na

The following preparations illustrate typical methods of preparing the compounds of this invention.

Compound 2.—2-(β -sulfoethylcarbamyl)-N-2-methyl-N- β -sulfoethylamino)phenyl)-1,4-naphthoquinoneimine dipotassium salt.—Salt: A solution of 59 g. of 2-(β -sulfoethylcarbamyl)-1-naphthol and 52 g. of 2-methyl-4-(N-ethyl-N- β -sulfoethylamino)aniline in 8 liters of 0.125 M tripotassium phosphate was treated with dilute hydrochloric acid with stirring, until the naphthol just began to precipitate (pH 8–9). Potassium ferricyanide (0.8 mole) in 1.6 liters of water was slowly added, with vigorous stirring, to form the dye. Sufficient barium chloride in water was slowly added to precipitate the inorganic salts. Excess barium chloride was added to the filtered solution, the precipitated dye salt was collected (suction) and treated with 10 liters of hot water. The resulting mixture was filtered, the residue treated with an additional 5 liters of hot water, filtered, and the filtrates were combined. Cooling yielded 42 g. of product as barium salt. This was converted to the potassium salt by triturating in a hot solution of an equivalent amount of potassium sulfate. The barium sulfate, which separated, was filtered off. The filtrate was concentrated and chilled whereupon the product separated as the potassium salt.

Compound 6.—2-aceto-N-(2-methyl-4-(N-ethyl-N- β -sulfoethylamino)phenyl)-1,4-naphthoquinoneimine sodium salt.—To a rapidly stirred, two-phase system of 1 liter of 2-butanone and 1 liter of 5% aqueous sodium bicarbonate containing 37 g. of 2-aceto-1-naphthol and 52 g. of 2-methyl-4-(N-ethyl-N- β -sulfoethylamino)aniline, was added, in portions, four molar equivalents (0.8 mole) of potassium ferricyanide in 1.6 liters of water. The phases were separated and the aqueous phase was re-extracted with 1 liter of 2-butanone to remove all the dye. The extracts were washed with 2 liters of sodium chloride solution (120 g./l.) and treated with 2,2,4-trimethylpentane to force out the residual water containing the dye as a separate phase. The aqueous solution containing the dye was separated and concentrated in vacuo. The residual solid dye was recrystallized from methyl alcohol to yield 40 g. of product.

The following examples are intended to illustrate our invention but not to limit it in any way.

EXAMPLE 1

A single layer photographic element was prepared by coating on a gelatin-subbed cellulose acetate film support the following layer:

A coating of a blue-sensitive developing-out negative gelatino-silver bromiodide (2.8 mole percent iodide) emulsion was coated at a coverage of 50 mg. of silver per square foot and 400 mg. of gelatin per square foot. The

layer also contained 50 mg. per square foot of the magenta coupler, 1-(2,5-dichlorophenyl)-3-[3-(4-t-amylphenoxy)benzamido]-5-pyrazolone, and 120 mg. per square foot of developing agent precursor, compound #1, of above table.

A sample of the above described coating was exposed to blue light through a negative and then processed by developing said sample for 3 minutes at 75° F. in contact with an unhardened gelatin coating (i.e. a suitably subbed cellulose acetate film support which contained 900 mg. per square foot of gelatin) which had been soaked in an alkaline activator solution having a pH of 13. After this time, the processed strip was separated from the gelatin pad and treated as follows: (Process solution temperatures—70° F.)

	Minutes
Kodak Fixing Bath F-5	5
"Lange's Handbook of Chemistry," p. 1677, 1944, Handbook Publishers, Sandusky, Ohio	
Water wash	5
At this point the strip contained an imagewise distribution of metallic silver together with the magenta dye image which was formed as the direct result of the coupling of the oxidized form of p-phenylenediamine developer with the incorporated magenta coupler. This strip was further processed as follows:	
Bleach (potassium bromiodide-ferricyanide)	8
Water wash	3
Kodak F-5 fix	5
Water wash	10
Air dry.	

After the above mentioned bleach and subsequent fix, only a magenta dye image remained in the coating.

EXAMPLE 2

The above experiment is repeated except that an amount equivalent to the amount of compound 1 of compound 7 is dispersed in 2 parts of 2,4-dinormal amyl phenol. Results equivalent to those obtained in Example 1 are obtained.

EXAMPLE 3

A multilayer color photographic element having the structure substantially as shown in the figure of the drawing is prepared by coating on a gelatin-subbed cellulose acetate opaque white film support the following layers numbered in sequence from the support:

(1) Developing agent precursor and antihalation layer¹

¹ In addition to being a developing agent precursor, this compound (i.e. compound #3) also serves as a cyan colored antihalation dye. This eliminates the need to use any other antihalation material (e.g. neutral colloidal silver) in this layer.

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(e.g. layer No. 11 of the figure).—A gelatin layer containing 600 mg. per square foot of gelatin and 500 mg. per square foot of compound #3 of above table.

(2) *Red-sensitive emulsion layer* (e.g. layer 12 of the figure).—A coating of a developing-out negative gelatino-silver bromiodide (6 mole percent iodide) emulsion sensitized to red light is coated at a coverage of 165 mg. of gelatin per square foot and 99 mg. of silver per square foot. The layer also contains 90 mg. per square foot of the cyan coupler, 1-hydroxy-N-[δ -(4-tert-amyl-2-butylphenoxy)-butyl]-2-naphthamide.

(3) *Interlayer* (e.g. layer No. 13 of the figure).—A gelatin layer coated at a coverage of 51 mg. per square foot.

(4) *Green-sensitive emulsion layer* (e.g. layer No. 14 of the figure).—A coating of a developing-out negative gelatino-silver bromiodide (2.8 mole percent iodide) emulsion sensitized to green light is coated at a coverage of 135 mg. of gelatin per square foot and 136 mg. of silver per square foot. The layer contains 90 mg. per square foot of the magenta coupler, 1-(2,5-dichlorophenyl)-3-[3-(4-tert-amylphenoxy)-benzamido]-5-pyrazolone.

(5) *Yellow Carey Lea silver interlayer* (e.g. layer No. 15 of the figure).—A filter layer comprising gelatin at a coverage of 50 mg. per square foot and yellow Carey Lea silver at a coverage of 10 mg. per square foot.

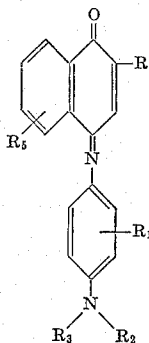
(6) *Blue-sensitive emulsion layer* (e.g. layer No. 16 of the figure).—A coating of a developing-out negative gelatino-silver bromiodide (2.8 mole percent iodide) emulsion is coated at a coverage of 188 mg. of gelatin per square foot and 140 mg. of silver per square foot. The layer contains 132 mg. per square foot of the yellow coupler, α -{4-[2,4-di-tert-amylphenoxyacetamido]benzoyl}-2-methoxyacetanilide.

A sample of the above mentioned coating is exposed to white light through a 3-color negative. This exposed sample is then processed according to the processes described in Example 1 above. An acceptable 3-color print is formed in this coating (i.e. dye images are formed in each of the three respective emulsion layers according to the silver records in same).

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An unexposed light sensitive silver halide emulsion having uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms),

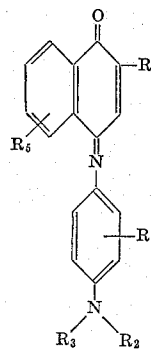
$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$
 $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl,

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$-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$

and $-\text{C}_6\text{H}_3(\text{COOH})_2$, R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16.

2. A photographic element comprising a support having thereon an unexposed light sensitive silver halide emulsion containing at least one color former, capable of reaction with the oxidation product of a primary aromatic amine color developer and integral therewith an alkali permeable layer containing uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:

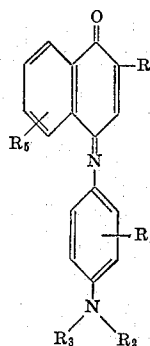


in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms),

$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$
 $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl,
 $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$

and $-\text{C}_6\text{H}_3(\text{COOH})_2$, R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16.

3. An unexposed light sensitive silver halide emulsion containing at least one color former capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and having uniformly dispersed therein a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and

—CONHR₄, wherein R₄ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms),

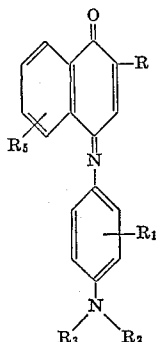
—CH₂CH₂SO₃H, —CH₂CH₂OH, —CH₂CH₂COOH

—CH₂CH₂NHSO₂CH₃, —CH₂CH₂SO₂NHCH₃, phenyl, 5

—C₆H₄SO₃H, —C₆H₄COOH, —C₆H₃(OH)₂

and —C₆H₃(COOH)₂, R₁ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R₂ and R₃ are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R₅ is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R, R₁, R₂, R₃ and R₅ is less than 16.

4. A multilayer photographic element having at least one layer comprising an unexposed light sensitive silver halide emulsion containing at least one color coupler capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and containing in at least one layer uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of —COCH₃, —COOC₂H₅ and —CONHR₄, wherein R₄ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), 40

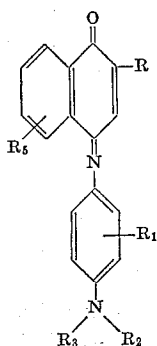
—CH₂CH₂SO₃H, —CH₂CH₂OH, —CH₂CH₂COOH

—CH₂CH₂NHSO₂CH₃, —CH₂CH₂SO₂NHCH₃, phenyl, 45

—C₆H₄SO₃H, —C₆H₄COOH, —C₆H₃(OH)₂

and —C₆H₃(COOH)₂, R₁ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R₂ and R₃ are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R₅ is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R, R₁, R₂, R₃ and R₅ is less than 16.

5. A photographic element comprising a support having thereon an unexposed light sensitive silver halide emulsion layer having a contiguous layer containing uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of —COCH₃, —COOC₂H₅ and —CONHR₄, wherein R₄ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms),

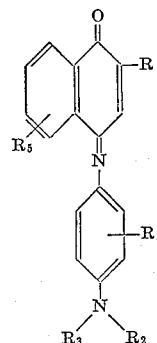
—CH₂CH₂SO₃H, —CH₂CH₂OH, —CH₂CH₂COOH

—CH₂CH₂NHSO₂CH₃, —CH₂CH₂SO₂NHCH₃, phenyl, 10

—C₆H₄SO₃H, —C₆H₄COOH, —C₆H₃(OH)₂

and —C₆H₃(COOH)₂, R₁ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R₂ and R₃ are selected from the class consisting of alkyl (1-4 carbon atoms), and substituted alkyl and R₅ is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R, R₁, R₂, R₃ and R₅ is less than 16.

6. A multilayer photographic element comprising a support and at least one unexposed photographic silver halide emulsion layer sensitive to the blue region of the spectrum, at least one unexposed photographic silver halide emulsion spectrally sensitized to the green region of the spectrum and at least one unexposed silver halide photographic emulsion spectrally sensitized to the red region of the spectrum, and containing in at least one layer of said multilayer element a light sensitive silver halide emulsion having uniformly dispersed therein a paraphenylenediamine precursor having the following general formula: 30



in which R is an electron withdrawing group selected from the class consisting of —COCH₃, —COOC₂H₅ and —CONHR₄, wherein R₄ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), 50

—CH₂CH₂SO₃H, —CH₂CH₂OH, —CH₂CH₂COOH

—CH₂CH₂NHSO₂CH₃, —CH₂CH₂SO₂NHCH₃, phenyl, 55

—C₆H₄SO₃H, —C₆H₄COOH, —C₆H₃(OH)₂

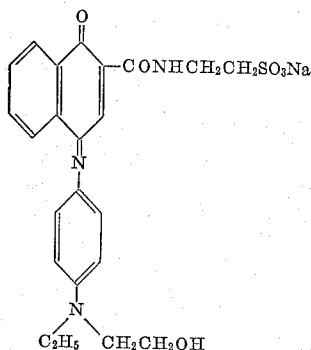
and —C₆H₃(COOH)₂, R₁ is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R₂ and R₃ are selected from the class consisting of alkyl (1-4 carbon atoms), and substituted alkyl and R₅ is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R, R₁, R₂, R₃ and R₅ is less than 16.

7. An unexposed light sensitive silver halide emulsion containing uniformly dispersed therein, 2-(β-sulfoethyl-carbamyl) - N - (2-methyl - 4 - (N-ethyl-N-β-sulfoethyl-amino)phenyl) - 1,4 - naphthoquinone imine dipotassium salt. 70

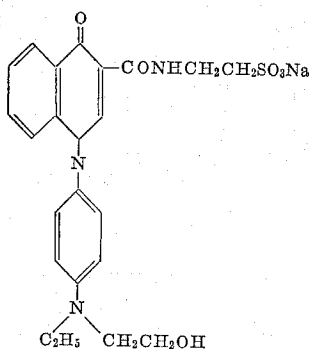
8. An unexposed light sensitive silver halide emulsion containing uniformly dispersed therein, 2-aceto - N - (2-methyl - 4 - (N-ethyl-N - β - sulfoethylamino)phenyl) 1,4 - naphthoquinone imine sodium salt. 75

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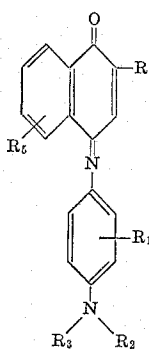
9. An unexposed light sensitive silver halide emulsion containing uniformly dispersed therein:



10. A multilayer photographic element having at least one unexposed light sensitive silver halide emulsion layer containing at least one color coupler capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and containing in at least one layer uniformly dispersed therein:



11. A process for developing an exposed light sensitive silver halide emulsion containing uniformly dispersed therein a paraphenylenediamine precursor having the following general formula:



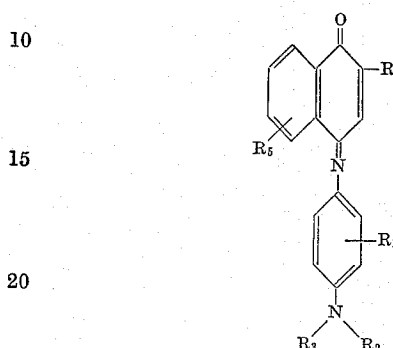
in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms),

$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl, $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and $-\text{C}_6\text{H}_3(\text{COOH})_2$

R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl, and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the emulsion under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

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12. A process for developing a photographic element comprising a support having thereon an exposed light sensitive silver halide emulsion containing at least one color former capable of reaction with the oxidation product of a primary aromatic amine color developer and integral therewith an alkali permeable layer containing uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:

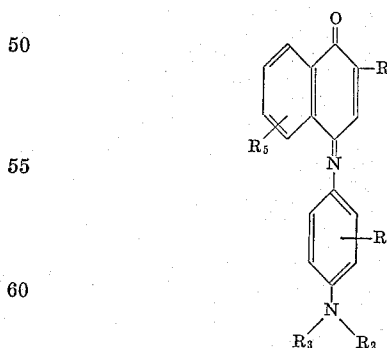


in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms)

$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl, $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and $-\text{C}_6\text{H}_3(\text{COOH})_2$

R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms) substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the element under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

13. A process for developing an exposed light sensitive silver halide emulsion containing at least one color former capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and uniformly dispersed therein a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms)

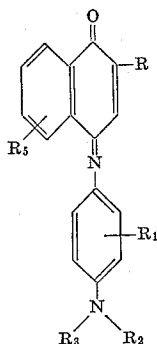
$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$, $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl, $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and $-\text{C}_6\text{H}_3(\text{COOH})_2$

R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and sub-

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stituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the emulsion under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

14. A process of developing an exposed multilayer photographic element having in at least one layer a light sensitive silver halide emulsion containing at least one color coupler capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and containing in at least one layer uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:

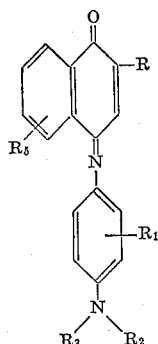


in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$, wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms)

$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$
 $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl
 $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and
 $-\text{C}_6\text{H}_3(\text{COOH})_2$

R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the element under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developer agent.

15. A process for developing a photographic element comprising a support having thereon an exposed light sensitive silver halide emulsion layer having a contiguous layer containing uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$ wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms)

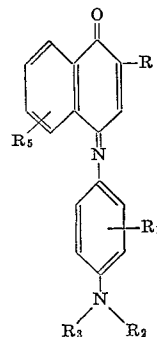
$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$
 $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl

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$-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and
 $-\text{C}_6\text{H}_3(\text{COOH})_2$

R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the element under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

16. A process for developing a multilayer photographic element comprising a support and at least one exposed photographic silver halide emulsion layer sensitive to the blue region of the spectrum, at least one exposed photographic silver halide emulsion spectrally sensitized to the green region of the spectrum and at least one exposed silver halide photographic emulsion spectrally sensitized to the red region of the spectrum, and containing in at least one layer of said multilayer element a light sensitive silver halide emulsion containing uniformly dispersed therein, a paraphenylenediamine precursor having the following general formula:



in which R is an electron withdrawing group selected from the class consisting of $-\text{COCH}_3$, $-\text{COOC}_2\text{H}_5$ and $-\text{CONHR}_4$ wherein R_4 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms)

$-\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$, $-\text{CH}_2\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_2\text{COOH}$
 $-\text{CH}_2\text{CH}_2\text{NHSO}_2\text{CH}_3$, $-\text{CH}_2\text{CH}_2\text{SO}_2\text{NHCH}_3$, phenyl
 $-\text{C}_6\text{H}_4\text{SO}_3\text{H}$, $-\text{C}_6\text{H}_4\text{COOH}$, $-\text{C}_6\text{H}_3(\text{OH})_2$, and
 $-\text{C}_6\text{H}_3(\text{COOH})_2$

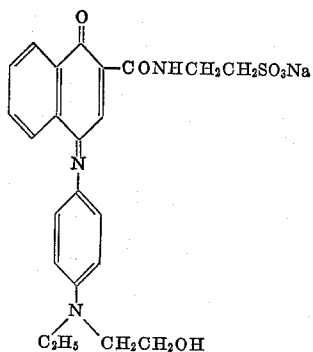
R_1 is selected from the class consisting of hydrogen, alkyl (1-4 carbon atoms), substituted alkyl, alkoxy and substituted alkoxy groups, R_2 and R_3 are selected from the class consisting of alkyl (1-4 carbon atoms) and substituted alkyl and R_5 is selected from the class consisting of hydrogen and solubilizing groups such that the total number of carbon atoms comprising R , R_1 , R_2 , R_3 and R_5 is less than 16, comprising activating the element under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

17. A process for developing an exposed light sensitive silver halide emulsion containing uniformly dispersed therein, 2 - (β - sulfoethylcarbamyl)-N-(2-methyl-4-(N-ethyl - N - β -sulfoethylamino)phenyl)-1,4-naphthoquinone imine dipotassium salt, comprising activating the emulsion under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

18. A process for developing an exposed light sensitive silver halide emulsion containing uniformly dispersed therein, 2 - aceto - N - (2-methyl-4-(N-ethyl-N- β -sulfoethylamino)-phenyl)-1,4-naphthoquinone imine sodium salt, comprising activating the emulsion under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

19. A process for developing an exposed light sensitive silver halide emulsion containing uniformly dispersed therein,

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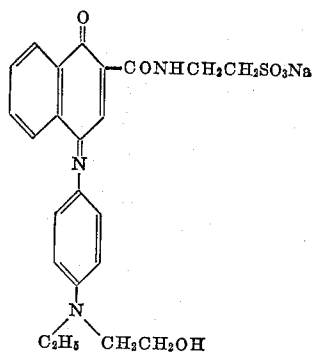


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comprising activating the emulsion under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

20. A process for developing a multilayer photographic element having at least one exposed light sensitive silver halide emulsion layer containing at least one color coupler capable of reaction with the oxidation product of a primary aromatic amine color developer to form a dye and containing in at least one layer uniformly dispersed therein

comprising activating the element under alkaline conditions to cleave the precursor and provide a p-phenylenediamine developing agent.

References Cited

UNITED STATES PATENTS

3,185,567 5/1965 Rogers ----- 96-95

NORMAN G. TORCHIN, *Primary Examiner*.

C. E. DAVIS, *Assistant Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,342,597

September 19, 1967

Donald P. Harnish et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 11, for " R_2 " read -- R_1 --; column 4, line 58, for "amplyhenoxy" read -- amylphenoxy --; column 5, line 44, for "alubumin" read -- albumin --; column 6, line 16, for "ethlidene" read -- ethylidene --; columns 7 and 8, in the table, second column, line 3 thereof, for " $\text{CONHCN}_2\text{CH}_2\text{SO}_3\text{Na}$ " read -- $\text{CONHCH}_2\text{CH}_2\text{SO}_3\text{Na}$ --; column 10, line 12, for "cootaining" read -- containing --.

Signed and sealed this 12th day of November 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents