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SILVER DYE BLEACH ELEMENT CONTAINING BALLASTED PARA-QUINONE AS DIFFUSION INHIBITOR

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No Drawing. Continuation-in-part of application Ser. No. 481,082, Aug. 19, 1965. This application Apr. 22, 1966, Ser. No. 544,387

Int. Cl. G03c 1/10, 7/00

U.S. Cl. 96—53

12 Claims

ABSTRACT OF THE DISCLOSURE

Silver-dye-bleach elements that exhibit reduced inter-image effects, reduced dye-image contrast, reduced migration of dye-bleach catalyst, reduced dye-image graininess and increased dye-image density are prepared by incorporating a diffusion inhibitor, such as a ballasted para-quinone, in one or more hydrophilic colloid layers such as colloid interlayers or colloid layers that also contain, if desired, the silver halide emulsion, bleachable dye or combinations of both. Additionally, the removal of developed silver metal is accomplished using milder bleaching solutions and shorter processing cycles.

This application is a continuation-in-part of Wilson, Nicholas and Williams U.S. patent application Ser. No. 481,082, filed Aug. 19, 1965, now abandoned.

This invention relates to photography, and more particularly to silver-dye-bleach processes and elements.

One common form of the silver-dye-bleach process employs a multilayer coating containing red, green, and blue-sensitized silver halide emulsion layers with bleachable cyan, magenta, and yellow dyes in or beneath the respective layers. After exposure to a light image, the material is developed in a black-and-white silver halide developing solution and then treated with a bleaching solution, containing a bleach catalyst, which oxidizes the metallic silver, i.e., the silver image. If desired, the bleach catalyst may be incorporated directly in the photographic element, e.g., either in an emulsion layer thereof or in a hydrophilic colloid layer contiguous to an emulsion layer. In oxidizing the silver, the catalyst is reduced in silver image areas. In its reduced form, the catalyst accelerates bleaching of dye in areas where dye and catalyst are present. The dye should be bleached only in silver image areas. However, most of the useful dye-bleach catalysts are diffusible in hydrophilic colloid layers. When the catalyst, in its reduced form, diffuses in the system, undesirable bleaching of the dye occurs in non-image areas. This undesirable diffusing and bleaching may take place either in the layer in which the catalyst is reduced, or in other dye containing layers in the system. Therefore, it appears highly desirable to provide photographic elements useful in the dye-bleach system which avoid undesirable bleaching of dye in non-image areas by diffused, reduced catalyst.

Also, it is frequently desirable to modify the sensitometric characteristics, e.g., to change the effective speed or to reduce the contrast of silver-dye-bleach systems. Efforts have been made to accomplish these sensitometric changes by the use of auxiliary diffusing dyes in the processing solutions or by the use of special silver bleaching agents such as o-nitro-aniline, p-nitrosodimethylaniline, ferric ammonium sulfate and the like. None of these procedures has been completely successful because (1) their effect on the various layers in the silver-dye-bleach materials is not uniform; (2) the activity of the proposed

agents cannot be localized to desired areas; and (3) the agents themselves have not been sufficiently inert for incorporation in silver-dye-bleach elements.

We have found a class of compounds which can be used to mitigate both the undesirable bleaching of dye in non-image areas and to change the image-dye contrast. Unexpectedly, this class of compounds also functions to enhance removal of silver from silver-dye-bleach photographic elements during dye bleach processing. Thus, the silver bleaching step can be conducted with milder solutions and shorter times.

One object of this invention is to provide novel photographic elements useful in the silver-dye-bleach process which have substantially reduced inter-image effects, such as undesirable bleaching of dye in non-image areas.

Another object of this invention is to provide novel photographic elements useful in the silver-dye-bleach process which have reduced dye-image contrast.

A further object of this invention is to provide novel photographic elements useful in the silver-dye-bleach process which prevent undesirable migration of reduced dye-bleach catalyst from one light-sensitive layer to another light-sensitive layer.

Another object of this invention is to provide novel photographic elements useful in the silver-dye-bleach process which yield increased maximum density of dye images.

Still another object of this invention is to provide novel photographic elements useful in the silver-dye-bleach process which yield less grainy dye images and superior dye-image resolution.

Another object of this invention is to provide novel means for controlling contrast in photographic elements useful in the dye-bleach process.

A further object of this invention is to provide novel photographic silver-dye-bleach elements which give dye images of improved photographic quality.

Another object of this invention is to provide silver-dye-bleach elements in which the silver is readily removed by bathing in a mild bleach for a short time.

Other objects of this invention will be apparent from the disclosure herein and in the appended claims.

In accordance with one embodiment of this invention, undesirable diffusion of reduced dye-bleach catalyst is effectively inhibited by incorporating in photographic elements certain diffusion-inhibitors which will be defined more fully hereafter.

Both interlayer and intralayer diffusion of reduced dye-bleach catalyst is inhibited in multilayer photographic dye-bleach elements having hydrophilic colloid interlayers between the light-sensitive layers, by incorporating in such hydrophilic colloid layers the diffusion-inhibitors of this invention.

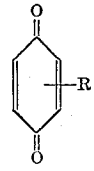
In another embodiment of this invention, photographic elements comprising a support having coated thereon silver halide dispersed in a hydrophilic colloid has incorporated in the hydrophilic colloid a bleachable dye and the novel diffusion-inhibitors of the invention. In a modification of this arrangement the bleachable dye is incorporated in a hydrophilic colloid coating contiguous to a silver halide emulsion layer, and the novel addenda of the invention are incorporated in either hydrophilic colloid layer, preferably the layer containing the silver halide. In these arrangements, the diffusion-inhibiting agents of the invention function not only to prevent diffusion of reduced dye-bleach catalyst through the system, but also to reduce contrast and graininess of the dye image.

In preferred embodiments, photographic elements suitable for providing multi-colored records are provided comprising silver halide emulsion layers sensitized to red, green and blue radiation, each of said layers having in-

corporated therein, respectively, bleachable cyan, magenta and yellow dye. The layers are advantageously coated in overlying relationship and are separated by hydrophilic colloid barrier layers. In preferred arrangements, a dye-bleach catalyst is incorporated in each light-sensitive layer together with an agent of the invention, which agent is also incorporated in each of the hydrophilic colloid interlayers separating the light-sensitive layers.

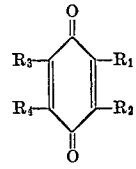
The diffusion-inhibiting agents which we employ in this invention have a half-wave potential greater than the dye-bleach catalyst employed, do not exercise detrimental effects on the photographic properties of the elements in which they are incorporated, and contain ballasting groups to prevent diffusion thereof through hydrophilic colloids. Preferably, these diffusion-inhibiting agents have a half-wave potential greater than about −0.10 volt. As employed herein, "half-wave potential" is determined by the method described in The Principles and Application of Polarography by G. W. C. Milner, Longmans, Green and Co., London, 1957, page 515 et. seq. and using a standard calomel electrode as the reference electrode.

Especially useful diffusion-inhibiting agents in accordance with this invention are ballasted para-quinones. Typical useful quinones include those having the formula:



wherein R represents a hydrocarbon substituent which prevents diffusion of the molecule in the hydrophilic colloid binder employed in the photographic element.

An especially useful class of diffusion-inhibitors are ballasted quinones having the formula:

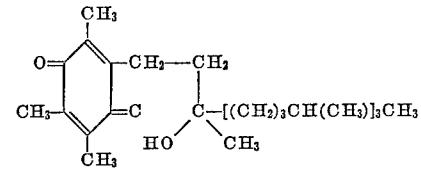


wherein R_1 represents a straight- or branched-chain, saturated or unsaturated aliphatic hydrocarbon substituent of from 1 to 30 carbon atoms, such as tert-butyl, tert-amyl, n-octyl, n-undecyl, n-hexadecyl, n-octadecyl, sec-octadecyl, pentacosyl, 3,7,11,15 - tetramethyl - 2 - hexadecenyl, 3-hydroxy-3,7-dimethyl-6-octenyl, and 3,7,11-trimethyl-2,6,10-dodecatrienyl, which substituent may have attached thereto a carboxyl or sulfo group, or an ammonium or alkali metal salt thereof, an aralkyl group, an acylamino group, such as acetamido, butyramido, [α-(2,4-di-t-amylphenoxy)acetamido]benzamido, α-(3-pentadecylphenoxy)butyr - amido, α - (4-t-butylphenoxy)-propionamido, 3,5-dicarboxybenzamido, etc.), a carbamyl group (e.g., N-methylcarbamyl, N-phenylcarbamyl, etc.), or a sulfamyl group (e.g., N-propylsulfamyl, N-tolylsulfamyl, etc.); R_2, R_3 and R_4 may represent hydrogen atoms, halogen atoms, carboxyl groups or sulfo groups and ammonium or alkali metal salts thereof, or R_2, R_3 and R_4 may, either one or severally, represent one of the groups described in R_1 above, for example, R_2 and R_3 may each represent a hydrogen atom and R_1 and R_4 may be one of the groups described in R_1 above, or R_3 and R_4 taken together may represent the atoms needed to form a six-membered ring. It will be understood that when a carboxyl or sulfo group is substituted directly on the quinone molecule, at least one other substituent on the quinone nucleus preferably is alkyl- or acyl-amino as described in R_1 above. The chain length or size of the alkyl and acylamino radicals can be widely varied depending on the degree of "ballasting" desired, one skilled in the art readily being able to ascertain the amount of ballasting needed for a particular purpose.

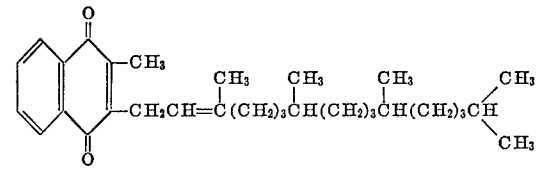
Alkyl radicals having 1 to 30 carbon atoms are suitable, although alkyl radicals having 8 to 22 carbon atoms are preferred. The number of carbon atoms in the ballast groups when totaled together advantageously is at least 10 carbon atoms per molecule of quinone.

The following are examples of compounds useful in the practice of our invention:

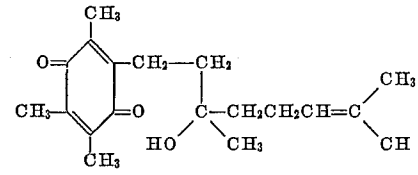
(1) 2-n-octadecyl-5-sulfobenzoquinone
(2) 2,5-di-n-octylbenzoquinone
(3) 2,5-di-n-undecylbenzoquinone
(4) 2-n-hexadecyl-5-sulfobenzoquinone potassium salt
(5) 2-n-octadecylnaphthoquinone
(6) 2 - {β - {3-[3-(4-amyl-x-sulfophenoxy)-benzamido]-benzamido}-ethyl}-quinone sodium salt
(7) 2,5 - bis{N-{3-[2,4-(diamylphenoxy)-5-(2-sulfobenzamido) - benzamido]-phenyl}-carbamylmethyl}quinone sodium salt
(8) 5-octadecyl-2-(2-sulfo-tert-butylquinone sodium salt
(9) 5-sec-octadecyl-2-(2-sulfo-tert-butyl)quinone sodium salt
(10) 2,5 - bis{β - [3-(p-tert-amylphenoxy-xsulfo]-benzamidoethyl}quinone sodium salt
(11) 2 - [2' - (2'',4''-di-tert-amylphenoxy)-5'-(3'',5''-disulfobenzamido)-benzamido]quinone sodium salt
(12) Sec-undecyl quinone-x-sulfonic acid potassium salt
(13) n-hexadecylquinone-x-sulfonic acid potassium salt
(14) n-Octadecylquinone-x-sulfonic acid potassium salt
(15) 2-methyl-5-sec-octadecylquinone-x-sulfonic acid potassium salt
(16) 2,5,6 - trimethyl-3-(3-hydroxy-3,7,11,15-tetramethylhexadecyl)benzoquinone



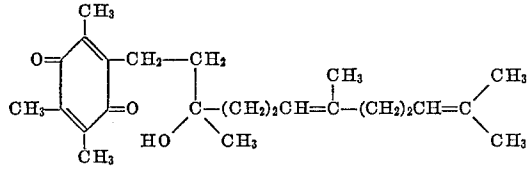
(17) 2-methyl-3-(3,7,11,15 - tetramethyl - 2 - hexadecenyl)-1,4-naphthoquinone



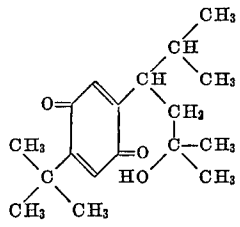
(18) 2,5,6-trimethyl - 3 - (3 - hydroxy-3,7-dimethyl-6-octenyl)benzoquinone



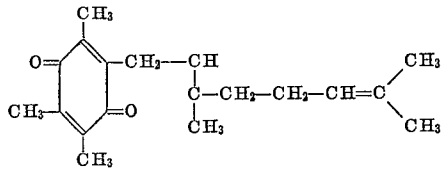
(19) 2,5,6 - trimethyl - 3 - (3 - hydroxy-3,7,11-trimethyl-6,10-dodecadienyl)benzoquinone



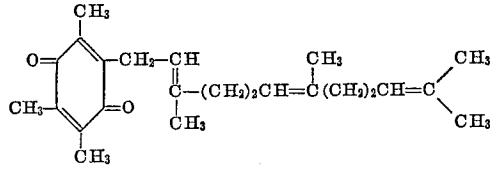
(20) 6-t-butyl-3-(1-isopropyl-3-hydroxy - 3 - methylbutyl) benzoquinone



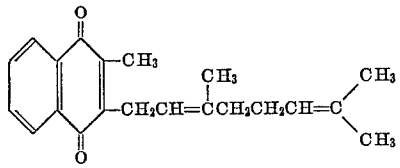
(21) 2,5,6-trimethyl - 3 - (3,7 - dimethyl-2,6-octadienyl) benzoquinone



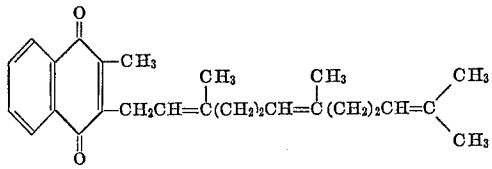
(22) 2,5,6-trimethyl-3-(3,7,11-trimethyl - 2,6,10 - dodecatrienyl)benzoquinone



(23) 2 - methyl - 3 - (3,7 - dimethyl-2,6-octadienyl)-1,4-naphthoquinone



(24) 2 - methyl-3-(3,7,11-trimethyl-2,6,10-dodecatrienyl)-1,4-naphthoquinone



The effective concentration of the novel agents of this invention varies over a broad range, and depends on the layer in which the agents are incorporated. The most useful range is from about 5 to 100 grams of agent per mole of silver. Relatively high concentrations may be desirable when the agents are employed in hydrophilic layers containing bleachable dye which do not contain silver halide, but are contiguous to a silver halide layer, in order to provide effective reduction in contrast and graininess of the dye image. Lower concentrations may be used to accomplish these functions when the agents are incorporated directly in the light-sensitive silver halide layer, whether that layer contains bleachable dye or the bleachable dye is in a contiguous layer. Lower concentrations may also be tolerated in lower layers in multi-layer coatings to effectively reduce contrast and graininess in those layers. When the agents of the invention are used in inter-layers to prevent diffusion of reduced catalyst, the most effective concentration will depend on the concentration of catalyst present in the element during processing. In multi-layer elements suitable for recording color images, dye image contrast may be controlled to improve color balance by employing differing concentrations of the agents of the invention which coact with the dye-bleach catalyst.

In general the ballasted quinones employed in the invention may be prepared by conventional methods, e.g., catalytic oxidation of the corresponding hydroquinones, as described in Organic Reactions, vol. 4, John Wiley and Sons, New York, 1948, pages 305–361.

As used herein and in the appended claims, "ballasted" refers to molecules containing a substituent which prevents diffusion of the molecules in the hydrophilic colloid employed in the photographic element.

In general, our compounds may be incorporated in inter-layers or emulsion layers by known methods such as direct dispersion or dispersing a solution of the quinone in an oily monomeric solvent of the type used in preparing color coupler dispersions, such as tri-o-cresyl phosphate and di-n-butyl phthalate.

The bleachable dyes used in system containing the compounds of our invention may be incorporated directly by conventional methods in the light-sensitive layers or they may be dispersed in adjacent hydrophilic colloid layers.

As noted, the diffusion-inhibiting agents of the invention prevent destruction of dye in non-image areas of photographic dye-bleach materials caused by diffusion of reduced dye-bleach catalyst through the system. This invention is applicable to photographic elements which have dye-bleach catalyst incorporated in the element, for example directly in the light-sensitive layer or in a hydrophilic colloid layer contiguous to the light-sensitive layer.

Any effective concentration of catalyst may be employed. Good results are obtained with from 5 to 80 grams of catalyst per mole of silver. The invention is also applicable to photographic elements which do not have dye-bleach catalysts incorporated therein, but which are processed by a step which includes contacting the element with a dye-bleach catalyst. In both instances, the invention effectively prevents diffusion of dye-bleach catalysts in their reduced form in the hydrophilic colloid employed in the photographic element. Hence, the invention is broadly effective in photographic elements processed by a dye-bleach method which includes exposing the element; developing the silver halide to form a silver image; and, bleaching the dye in the silver image areas in the presence of a dye-bleach catalyst. Any compound is effective in catalyzing the bleaching of dye in this process, and which tends to diffuse in hydrophilic colloids, may be employed. Advantageously, the dye-bleach catalyst has a half-wave potential of between about −0.07 to −0.24 volt. Any compound useful for catalyzing dye destruction in the dye-bleach process may be employed. Phenazine and quinoxaline compounds are especially useful catalysts. Some particularly useful catalysts are listed below:

Phenazine
2-hydroxy-3-aminophenazine
2-anthraquinone sulfonic acid (Na salt)
2-methyl-3-(p-nitrophenyl)quinoxaline
2-methyl pyrazine
2-carbamyl pyrazine
2,3,5,6-tetramethyl pyrazine
Quinoxaline
2-methyl quinoxaline
6-chloro quinoxaline
6-nitro quinoxaline
6-methyl quinoxaline

6-methoxy quinoxaline
6,7-dimethyl quinoxaline
2,3-bis(2-methyl-6-pyridyl)-6,7-dimethyl quinoxaline
6,7-dimethyl-2,3-diphenyl quinoxaline
6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline
2,3-diphenyl-6-nitrol quinoxaline
2,3,6,7-tetramethyl quinoxaline
2,3-dimethyl quinoxaline
2,3-diphenyl quinoxaline
4-hydroxypteridine
6,7-dimethyl-4-hydroxy-2-mercaptoteridine
2,3(1,8-naphthyl) quinoxaline
2-carbethoxy-3-methoxy quinoxaline

Other useful catalysts are disclosed in the following U.S. Patents: 2,183,395; 2,669,517; 2,627,461; 2,578,710; 2,541,884; 2,410,025; 2,348,894, 2,341,034 and 2,270,118.

As employed herein and in the appended claims, the term "in association therewith" refers to elements wherein the diffusion-inhibitor, catalyst, bleachable-dye or other addendum is present either directly in a light-sensitive silver halide emulsion layer, or in a layer, preferably a hydrophilic colloid layer, contiguous to the light-sensitive silver halide emulsion layer. Development of the elements of the invention is preferably conducted at a pH of about 9 to 12.0.

Our invention is illustrated further by the examples that follow.

EXAMPLE 1

Element A

A multilayer element for the production of a color image by the silver-dye-bleach process was prepared having the following structure and composition:

	Mg./ft.[2]
Layer 8:	
Blue-sensitive silver halide emulsion:[1]	
Silver	108
Gelatin	80
Layer 7:	
Gelatin	100
Yellow dye [2]	35
Mordant [3]	100
Layer 6:	
Gelatin	100
Di-n-octylquinone [4]	40
Layer 5:	
Green-sensitive silver halide emulsion: [1]	
Silver	108
Gelatin	80
Layer 4:	
Gelatin	90
Magenta dye [5]	26
Mordant [3]	66
Layer 3:	
Gelatin	100
Di-n-octylquinone [4]	40
Layer 2:	
Red-sensitive silver halide emulsion: [1]	
Silver	108
Gelatin	80
Layer 1:	
Gelatin	120
Cyan dye [6]	21
Mordant [3]	51
Cellulose acetate support	

Element B

A multilayer coating was prepared which was identical in all respects to Element A except that it did not contain the di-n-octylquinone in Layers 3 and 6.

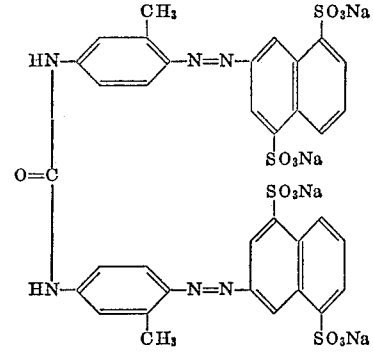
A sample of each of Elements A and B was sensitometrically exposed on an Eastman IB sensitometer for 1/100 second to a 500-watt lamp, 3000° K., through a 2B (red) filter and processed as follows:

(1) Develop to a silver image by 1.5 minutes treatment in Kodak D-72 developer modified with 2.0 g. of potassium thiocyanate and 10.0 ml. of 0.5% 5-methylbenzotriazole in water
(2) Rinse 30 seconds
(3) Treat for 1 minute in Kodak F-5 fixing solution
(4) Rinse 30 seconds
(5) Dye-bleach for 30 second in the following bath:

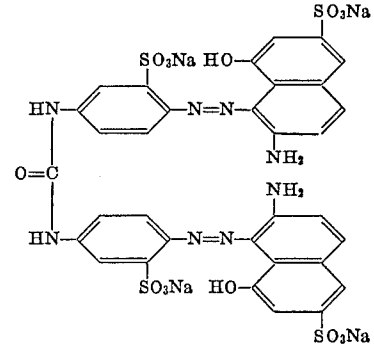
Hydrochloric acid (conc.) ml	100
2-hydroxy-3-aminophenazine mg	150
Thiourea g	100
Distilled water ml	775
Distilled water to make 1 liter	

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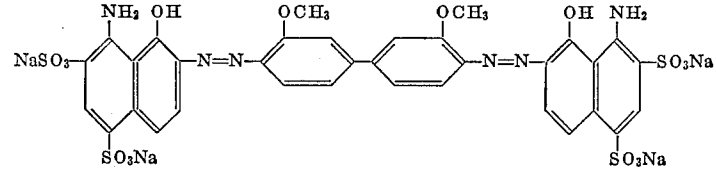
[1] AgBrI emulsion (containing 10.6 mole percent iodide).
[2] Yellow dye: Solantine Yellow RL (Color Index 29025).



[3] Mordant: Poly-α-methylallyl-N-guandanidylketimine, glycolic acid salt.
[4] Prior to its addition to the coating composition, the ballasted quinone, di-n-octylquinone, had been dispersed in the solvent di-n-amylphenol at a ratio, by weight, of quinone to solvent of 1:3. Di-n-octylquinone serves in this coating to inhibit diffusion of reduced dye-bleach catalyst.
[5] Magenta dye: Solantine Pink 4BL (Color Index 25,380).



[6] Cyan dye: Niagara Sky Blue (Color Index 24,400)



The 2-hydroxy-3-aminophenazine was dissolved separately in a mixture of 15 ml. of distilled water and 15 ml. of glacial acetic acid, and the resulting solution was then added to the above composition of thiourea, hydrochloric acid and water.

(6) Rinse 30 seconds

(7) Silver-bleach for 1 minute in the following bath:

$CuCl_2 \cdot 2H_2O$	g	100
Hydrochloric acid (conc.)	ml	25
Water to make 1 liter		

(8) Rinse 30 seconds

(9) Fix in Kodak F–5 solution for 1 minute

(10) Wash for 3 minutes and dry.

The red patches of the color charts formed in each of the above coatings were compared. In the control sample (Element B), very little magenta or yellow dye was formed because reduced bleach catalyst, diffusing from the red-sensitive layer, reduced the magenta dye in the layer immediately below the green-sensitive layer, as well as the yellow dye in the layer immediately below the blue-sensitive layer. In the coating containing ballasted diffusion-inhibiting compound in the gelatin interlayers (Element A), said compound prevented diffusion of the reduced bleach catalyst into neighboring dye layers. Consequently, no undesirable reduction of dye in these layers occurred.

EXAMPLE 2

The following four single-layer coatings were prepared on a cellulose acetate film support with a silver halide emulsion as described in Example 1.

Coating 1:	Mg./ft.^{2}
Silver	108
Gelatin	203
Mordant (described in Example 1)	63
Cyan dye (described in Example 1)	26
Di-n-octylquinone	None
Coating 2:	
Same as Coating 1, plus:	
Di-n-octylquinone	20
Coating 3:	
Same as Coating 1, plus:	
Di-n-octylquinone	40
Coating 4:	
Same as coating 1, plus:	
Di-n-octylquinone	80

Each coating was identically exposed through a 0.3 Log E neutral density step tablet, developed for 3 minutes in the developer described in Example 1, and then processed according to the procedure outlined in Example 1.

A sensitometric evaluation of each processed sample yielded the following results.

	Contrast	D_{max}	D_{min}
Coating 1	2.24	0.56	0.02
Coating 2	1.82	1.12	0.03
Coating 3	1.62	1.21	0.03
Coating 4	1.41	1.32	0.04

A comparison of the above recorded results indicates that, with retention of essentially the same low D_{min}, lower contrasts and higher dye yields were obtained with the elements containing the ballasted quinone.

EXAMPLE 3

A multilayer element was prepared similar in all respects to that of Example 1 except that the ballasted quinone was incorporated directly in the light-sensitive layers, 2, 5 and 8 and the interlayers 3 and 6 were omitted from the coating. The quinone employed was compound 2.

A similar multilayer coating, which did not contain any ballasted quinone, was the control.

The samples were exposed and processed in the manner of Example 2. Results similar to those of Example 2 were obtained.

EXAMPLE 4

Results similar to those in Example 1 were obtained when compounds 2, 4 and 6 respectively were used as diffusion-inhibiting compounds in interlayers of a multilayer element such as described in Example 1.

EXAMPLE 5

Element A

A multilayer element was prepared similar in all respects to that described in Example 1, except that no di-n-octylquinone was contained in Layers 3 and 6, and that Layers 2, 5 and 8, respectively, each contained 35 mg./ft.^{2} of the ballasted quinone, Compound 16 according to this invention.

Element B

An element similar to the above Element A was prepared with the omission of the ballasted quinone in Layers 2, 5 and 8, respectively.

Each of the Elements A and B was exposed and processed according to the manner described in Example 1 above.

The results obtained were similar to those described in Example 1. Similar results were obtained when the tests described in Example 5 were repeated using Compound 17, 19, 21, 23 and 24, respectively.

EXAMPLE 6

Coating A

A photographic support was overcoated with a silver chlorobromide gelatin emulsion to contain per square foot of dried film:

Layer 1:	Mg.
Gelatin	300
Silver	108
Mordant (described in Example 1)	105
Di-pyridolquinoxaline [1]	15

Coating B

A two-layer coating was prepared on a separate support to have the following structure and composition upon drying:

Layer 2:	Mg.
Gelatin	200
Compound 16	76
Layer 1:	
Gelatin	300
Solantine yellow dye (described in Example 1)	60
Mordant (described in Example 1)	150
Support	

Coating C

A two-layer coatng was prepared identical in all respects to Coating B except that Compound 16 was omitted from Layer 2.

Two 35 mm. strips of Coating A were identically exposed in an Eastman IB sensitometer through a 0.3 Log E neutral density step tablet and developed for 1.5 minutes at a temperature of 68° in the modified Kodak D–72 developing solution described in Example 1 above.

Coatings B and C were dipped for 15 seconds in a dye-bleach activator as described in Example 1 and then squeegeed together for 5 minutes with either strip of Coating A, respectively. After separation, Coatings B and C were washed for 5 minutes in cold water and dried. The two strips of Coating A were fixed for 1 minute, then washed and dried. The results obtained were as follows:

(a) The dye in Coating B was not bleached, and the silver image on the strip of Coating A which had been in contact with Coating B was completely removed.

(b) The dye in Coating C was completely bleached in areas which had been opposite the image portion of the contacted strip of Coating A, and the silver images on Coating A had essentially retained their initial densities.

The above results illustrate the effectiveness of the ballasted quinones according to our invention with respect to

(a) blocking the migration of reduced bleach catalyst; and (b) oxidizing the reduced silver in the image areas.

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. In a photographic element comprising a support having coated thereon a light-sensitive dispersion of silver halide in a hydrophilic colloid binder, and having in association therewith a bleachable dye, said element being suitable for use in a silver-dye-bleach process which comprises exposing the photographic element; developing the silver halide to form a silver image; and, bleaching the dye in the silver image areas in the presence of a dye-bleach catalyst, which catalyst, at least in its reduced form, tends to diffuse in hydrophilic colloid layers and cause bleaching of dye in non-image areas: the improvement in said element which comprises having in said hydrophilic colloid binder an effective concentration of a ballasted para-quinone which both reduces dye-image contrast and inhibits diffusion of said reduced catalyst, said ballasted para-quinone having a half-wave potential greater than the dye-bleach catalyst used in processing said element, said ballasted para-quinone being substantially non-diffusible in said hydrophilic colloid and free from detrimental effects on the light-sensitive materials in said photographic element.

2. In a photographic element comprising a support having coated thereon a plurality of layers comprising silver halide dispersed in a hydrophilic colloid, said layers having in association therewith bleachable dye, said element being suitable for use in a silver-dye-bleach process which comprises exposing said element; developing a negative silver image in said element; and bleaching said dye in areas of the silver image in the presence of a dye-bleach catalyst, which catalyst, at least in its reduced form, tends to diffuse through said hydrophilic colloid and bleach dye in non-image areas: the improvement in said elements which comprises having in at least one of said hydrophilic colloid layers an effective concentration of a ballasted para-quinone which both reduces dye-image contrast and graininess and inhibits diffusion of said reduced catalyst, said ballasted para-quinone having a half-wave potential greater than the dye-bleach catalyst used in processing said element, said ballasted para-quinone being substantially non-diffusible in said hydrophilic colloid and free from detrimental effects on the light-sensitive materials in said photographic element.

3. In a photographic element comprising a support having coated thereon at least two light-sensitive layers comprising silver halide dispersed in a hydrophilic colloid, said layers having in association therewith a bleachable dye, and said layers being separated by a non-light-sensitive hydrophilic colloid barrier layer, said element being suitable for use in a silver-dye-bleach process which comprises exposing said element; developing a silver image in said element; and, bleaching said dye in areas of the silver image in the presence of a dye-bleach catalyst, which catalyst, at least in its reduced form, tends to diffuse through said hydrophilic colloid and bleach dye in non-image areas: the improvement in said element which comprises having in said barrier layer an effective concentration of a ballasted para-quinone diffusion inhibitor which both reduces dye-image contrast and inhibits diffusion of said reduced catalyst, said ballasted para-quinone having a half-wave potential greater than the dye-bleach catalyst used in processing said element, said ballasted para-quinone being substantially non-diffusible in said hydrophilic colloid and free from detrimental effects on the light-sensitive materials in said photographic element.

4. In a photographic element comprising a support having coated thereon at least three separate light-sensitive layers comprising silver halide dispersed in a hydrophilic colloid, said layers being sensitized, respectively, to red, green and blue radiation and containing, respectively, bleachable cyan, magenta and yellow dye, each of said layers containing a dye-bleach catalyst which, at least in its reduced form, tends to diffuse through said hydrophilic colloid layers, the improvement in said element which comprises having in each of said layers an effective concentration of a ballasted para-quinone which both reduces dye-image contrast and graininess and inhibits diffusion of said reduced catalyst, said ballasted para-quinone having a half-wave potential greater than the dye-bleach catalyst used in processing said element, said ballasted para-quinone being substantially non-diffusible in said hydrophilic colloid and free from detrimental effects on the light-sensitive materials in said photographic element.

5. The photographic element of claim 4 wherein each of said light-sensitive layers are separated from one another by non-light-sensitive hydrophilic colloid barrier layers, said layers containing a ballasted para-quinone which is substantially non-diffusible in said hydrophilic colloid, said para-quinone being present in said barrier layer in a concentration effective to prevent inter-layer diffusing of reduced bleach catalyst.

6. The photographic element of claim 4 wherein the ballasted quinone is 2,5-di-n-octylbenzoquinone.

7. The photographic element of claim 4 wherein the ballasted quinone is 2-methyl-3-(3,7,11,15-tetramethyl-2-hexadecenyl)1,4-naphthoquinone.

8. The photographic element of claim 4 wherein the ballasted quinone is 2,5,6-trimethyl-3-(3-hydroxy-3,7,11-trimethyl-6,10-dodecadienyl)benzoquinone.

9. The photographic element of claim 4 wherein the ballasted quinone is 2,5,6-trimethyl-3-(3,7-dimethyl-2,6-octadienyl)benzoquinone.

10. The photographic element of claim 4 wherein the ballasted quinone is 2-methyl-3-(3,7,11-trimethyl-3,6,10-dodecatrienyl)-1,4-naphthoquinone.

11. In the silver-dye-bleach processing of a photographic element comprising a support having coated thereon a light-sensitive dispersion of silver halide in a hydrophilic colloid binder, and having an association therewith a bleachable dye, to prepare photographic dye images, which process comprises exposing the photographic element; developing the silver halide to form a silver image; and, bleaching the dye in the silver image areas in the presence of a dye-bleach catalyst, which catalyst, at least in its reduced form, tends to diffuse in hydrophilic colloid layers and cause bleaching of dye in non-imaged areas: the improvement in said process which comprises incorporating in a hydrophilic colloid layer a ballasted para-quinone having a half-wave potential greater than the dye-bleach catalyst used in processing said element, said ballasted para-quinone being substantially non-diffusible in said hydrophilic colloid and free from detrimental effects on the light-sensitive materials in said photographic element.

12. A process as described in claim 11 wherein said ballasted para-quinone is incorporated in a hydrophilic colloid layer having silver halide dispersed therein.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,457,074 Dated August 4, 1969

Inventor(s) Ransford B. Wilson, Robert D. Nicholas and Carl J. Willi

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

Column 11, line 42, the word "elements" should read ---element---.

Column 12, line 38, that portion of the formula reading 3,6,10 should read 2,6,10.

SIGNED AND
SEALED
FEB 17 1970

(SEAL)
Attest:

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Commissioner of Patents