

3,201,244

METHOD OF INHIBITING DISCOLORATION OF COLOR PHOTOGRAPHIC LAYERS CONTAINING DYE IMAGES AND RESULTING PHOTOGRAPHIC PRODUCTS

George W. Larson, Rochester, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

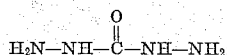
No Drawing. Filed Oct. 18, 1962, Ser. No. 231,587
5 Claims. (Cl. 96—56)

This invention relates to color photography and more particularly to methods for preventing discoloration of photographic dye images. The invention also includes photographic layers or elements stabilized against discoloration according to the new methods.

Photographic color images can be produced by a variety of processes. Perhaps the most common involves the formation of the desired color record by coupling between one or more color couplers and the oxidation products of an ordinary photographic color developing agent, such as a phenylenediamine. The color coupler in such processes can be incorporated either within the photographic element itself, or within the color developer solution. Another method of producing a color record involves the use of the well known dye bleach process, wherein a uniformly dyed layer is selectively bleached in accordance with a silver record produced through conventional photographic development. Bleaching occurs at the site of formation of the silver image. Still another means of producing a photographic color image is through a diffusion transfer process which uses a dye developer to effect photographic development and to produce a diffusible dye, which then migrates imagewise to a receiving surface. The present invention provides a means of stabilizing all of these types of photographic dye images, although it is particularly useful in preserving dye images which have been produced by the conventional process of color development using a color developer containing the color-forming compound, or coupler. This latter process is a reversal type of process wherein the color development is preceded by a conventional black-and-white development operation which produces a negative silver image. After negative development, there is one or more exposures followed by color development in a developer containing the desired color-forming compound, or coupler.

It is, therefore, an object of the present invention to provide an improved method for preventing the discoloration or decomposition of photographic layers containing dye images subject to fading, or print-out under the influence of actinic radiation. It is a further object to provide photographic color materials, including films, transparencies, or prints which have been stabilized by treatment with particular stabilizing compounds. Other objects will become apparent from a consideration of the following description and examples.

The foregoing objects are accomplished according to my invention by bathing the finished photographic record (i.e., after complete color-development, bleaching, fixation, etc.) with an aqueous solution containing carbonylhydrazide, either as the free base, or as a salt (in the form of a buffered solution). Carbonylhydrazide is a well known chemical and can be represented by the following formula:



It is, of course, known that multicolor photographs can be stabilized by a final bath containing urea, but I have found that the carbonylhydrazide of my invention

has rather substantial advantages over the urea of the prior art.

The system of three-color photography suggested by Fischer in U.S. Patent 1,055,155, issued March 4, 1913 forms the basis for a number of color photographic processes and products. In one embodiment, this process involves the incorporation of different color-forming coupler compounds in each of three superposed differently color-sensitized (red, green and blue) silver halide emulsion layers. Each of the three couplers is capable of producing a color complementary to the sensitivity of the layer in which is incorporated by reaction with the oxidation products of certain types of photographic developing agents. In this way a developed silver image and a colored dye image are formed simultaneously in each of the three superposed emulsion layers. The silver images and residual undeveloped silver halide may then be removed from the multilayer photographic element by bleaching, fixing and washing according to now well-known methods. Alternatively, the color-forming couplers can be incorporated in the developer rather than in the emulsion layers as disclosed in Fischer U.S. Patent 1,102,028, issued June 30, 1914.

The couplers suggested by Fischer containing phenolic hydroxyl, or ketomethylene groups, react with the oxidation products of aromatic amine developing agents during photographic development to form indophenol, indamine, indoaniline or azomethine (including quinonimine) dyes. Dyes produced by developing with amino-phenols in the presence of a phenol or naphthol coupler are indophenol dyes, those produced by developing with a phenylenediamine type developer in the presence of an aniline coupler, phenol or naphthol couplers, or reactive methylene compounds are indamine, indoaniline and azomethine dyes, respectively. Azomethine and indoaniline dyes are present in many of the processed photographic color products produced by current photographic processes.

While the process of Fischer U.S. Patent 1,055,155 in which the color-forming couplers are incorporated in the emulsion layers is theoretically feasible, it has not been entirely successful due to the tendency of the couplers to diffuse out of their respective emulsion layers during coating, or processing. For this reason, it has been proposed to react the coupler molecules with high molecular weight, or colloidal, bodies to render the couplers non-diffusing in gelatin or other colloidal media. It has also been proposed to mix the couplers with a water-insoluble colloid, such as a natural or synthetic resin, or a cellulose ester, and to subsequently disperse this mixture in the gelatin emulsion. Methods of this type are disclosed in Martinez U.S. Patent 2,269,158, issued January 6, 1942 and in Mannes and Godowsky U.S. Patents 2,304,939 and 2,304,940, issued December 15, 1942. These patents also disclose specific couplers adapted to be dispersed in emulsion layers as just described. Other couplers are disclosed in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957 and in Porter et al. U.S. Patent 2,369,489, issued February 13, 1945, as well as in numerous other patents, which use a water-soluble, crystalline, high-boiling solvent for the color coupler.

Specific couplers useful in photographic color processes in which the couplers are not dispersed in a water immiscible solvent are disclosed in the following representative references: Mannes and Godowsky U.S. Patent 2,039,730, issued May 5, 1936, hydroxy diphenyl couplers which form blue or blue-green dyes; Mannes and Godowsky U.S. Patent 2,108,602, issued February 15, 1938, acetoacetamides and cyanoacetamides, containing reactive

methylene groups, which form yellow dyes; Mannes and Godowsky U.S. Patent 2,115,394, issued April 26, 1938, organic compounds containing the cyanoacetyl group which form red and magenta dyes; and Richey and Jensen U.S. patent application Serial No. 670,900, filed July 10, 1957, water soluble cyan, magenta and yellow dye-forming couplers.

The developing agents useful for color development of emulsion layers containing couplers of the type described above or for the development of emulsion layers in the presence of these couplers include the well-known primary aromatic amine silver halide developing agents, such as the phenylenediamines, including the N-alkyl-phenylenediamines and N-alkyltolenylenediamines. These developing agents are usually used in the salt form, such as the hydrochloride, or sulfate, which is more stable than the amine. The p-aminophenols and their substitution products can also be used where the amino group is unsubstituted. The N-alkylsulfonamidoalkyl-p-phenylenediamine agents of Weissberger U.S. Patent 2,193,015, issued March 12, 1940, are also very useful. All of the developing agents have an unsubstituted amino group which enables the oxidation products of the developer to couple with the color-forming compounds to form a dye image.

Many indophenol, indamine, indoaniline and azomethine dyes are relatively unstable to light with the result that dye images in finished commercial color pictures have a tendency to fade, especially when subjected to intense illumination for extended periods of time. This is true whether the source of illumination is sunlight, tungsten or fluorescent lamps. The cyan dyes are generally relatively less susceptible to fading than the other dyes commonly used in color photography. In processes in which the couplers are incorporated in the emulsion layers or in plain gelatin layers in the film, further difficulty is caused by residual unused coupler which tends to print-out as a stain, usually a yellow stain, under the influence of light especially in the high light areas of the picture. Magenta dye-forming couplers are generally more susceptible to print-out than others.

In general, two methods have been suggested to prevent discoloration of photographic layers. One of these comprises overcoating the photographic layer to be protected with a substance capable of absorbing ultraviolet light. Methods of this type are disclosed in Salminen and Allen U.S. Patent 2,632,701, issued March 24, 1953, and Edgerton and Staud U.S. Patent 2,747,996, issued May 29, 1956. The other method referred to above comprises treatment of photographic layers containing dye images with certain chemical compounds, particularly organic reducing agents or antioxidants, in order to stabilize the dye images and any residual coupler in the photographic layer. Methods of this type are disclosed in Vittum U.S. Patent 2,384,658, issued September 11, 1955, and Mackey U.S. Patent 2,579,435, issued December 18, 1951. Methods of the latter type have been found to be mostly empirical. For example, although the reducing agents of the Vittum patent are useful, others of similar reducing properties have no effect on the stability of photographic dye images. Further, many reducing compounds which might suggest themselves as stabilizing agents not only have no stabilizing properties but actually cause strain or destruction of dye images in photographic layers. It has, therefore, been difficult to find compounds having appreciable dye stabilizing or anti-print-out properties which are also free from other undesirable characteristics. Therefore, although the above and other methods have been suggested in the art for protecting colored photographic elements against discoloration due to fading or print-out, none has proven to be a complete solution to the problem and the search for new methods has continued.

The methods of the present invention for preventing the

discoloration of water permeable photographic layers containing dye images comprise treating such layers with aqueous solutions of certain organic compounds in order to introduce sufficient quantities of these treating agents into the photographic layers to inhibit fading of the dye images or print-out of any residual dye-forming coupler therein. In practice, the photographic element or layer containing the dye image, but substantially free from developed silver, silver halide and other soluble salts, is immersed in a bath comprising an aqueous solution of one of the treating agents of the invention. The photographic layer is allowed to remain in the bath until it has absorbed sufficient treating solution to inhibit discoloration. The photographic layer is then removed from the bath and allowed to dry containing the absorbed treating agent. Optionally, surplus treating solution may be removed from the surface of the photographic element or layer by means of a squeegee, rapid water rinse or other suitable means prior to drying. When a water rinse is employed, however, care must be taken not to remove absorbed treating agent from the treated layer.

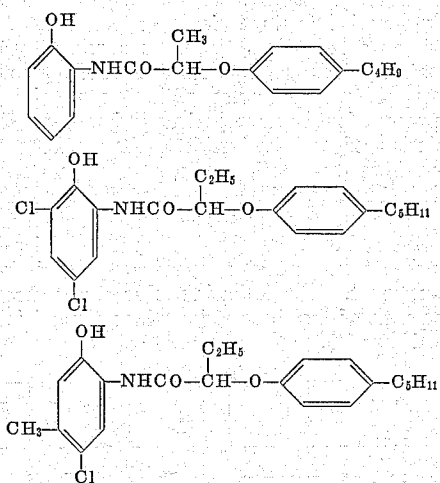
As indicated above, my invention is particularly useful in stabilizing photographic color images produced by a reversal color process wherein the color-forming components or couplers are incorporated within the photographic color developer. One of the most common of these processes is known as the Kodachrome Process. Especially useful color-forming compounds or couplers which can be incorporated in color developers include the following:

Couplers producing cyan images

- 5-(p-amyphenoxybenzenesulfonamino)-1-naphthol
- 5-(N-benzyl-N-naphthalenesulfonamino)-1-naphthol
- 5-(n-benzyl-N-n-valeryl-amino)-1-naphthol
- 5-caproylamino-1-naphthol
- 2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
- 2,4-dichloro-5-(p-nitrobenzoyl- β -o-hydroxyethylamino)-1-naphthol
- 2,4-dichloro-5-palmitylamino-1-naphthol
- 2,2'-dihydroxy-5,5'-dibromostilbene
- 5-diphenylethersulfonamido-1-naphthol
- 1-hydroxy-2-(N-isoamyl-N-phenyl)naphthamide
- 1-hydroxy-2-(N-p-sec. amyphenyl)naphthamide
- 8-hydroxy-1- α -naphthoyl-1,2,3,4-tetrahydroquinoline
- 2-lauryl-4-chlorophenol
- 1-naphthol-2-carboxylic- α -naphthalide
- 1-naphthol-5-sulfo-cyclohexylamide
- 5-phenoxyacetamino-1-naphthol
- 5- β -phenylpropionylamino-1-naphthol
- Monochloro-5-(N- γ -phenylpropyl-N-p-sec.-amylbenzoylamino)-1-naphthol
- 2-acetyl-amino-5-methylphenol
- 2-benzoylamino-3,5-dimethylphenol
- 2- α (p-tert. amyphenoxy)-n-butyrylamino-5-methylphenol
- 6-{ γ -[4- γ (2,4-di-tert. amyphenoxy)butyramido]phenoxy}acetamido-2,4-dichloro-3-methylphenol
- 1-hydroxy-2-[δ -(2,4-di-tert. amyphenoxy)-n-butyl]naphthamide
- 2- α (p-tert. amyphenoxy)-n-butyrylamino-4-chloro-5-methylphenol
- 2-(p'-tert. amyphenoxy-p-benzoyl)amino-4-chloro-5-methylphenol
- 2-(4'-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
- 2-phenylacetyl-amino-4-chloro-5-methylphenol
- 2-benzoylamino-4-chloro-5-methylphenol
- 2-anilinoacetyl-amino-4-chloro-5-methylphenol
- 2-{4'-[α -(4'-tert. amyphenoxy)-n-butyrylamino]benzoylamino}-4-chloro-5-methylphenol
- 2-[4',3''-(4'''-tert. amyphenoxy)benzoylamino]benzoylamino-4-chloro-5-methylphenol
- 2-p-nitrobenzoylamino-4-chloro-5-methylphenol
- 2-m-aminobenzoyl-4-chloro-5-methylphenol
- 2-acetamino-4-chloro-5-methylphenol

2-(4'-sec. amylbenzamino)-4-chloro-5-methylphenol
 2-(4'-n-amyoxybenzamino)-4-chloro-5-methylphenol
 2-(4'-phenoxybenzoylamino)phenol
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
 2-[α -(4'-tert. butylphenoxy)propionylamino]phenol
 2-[α -(4'-tert. amyl)phenoxypropionylamino]phenol
 2-[N-methyl-N-(4''-tert. amyl-3'-phenoxybenzoyl-amino)]phenol
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-methyl-1-phenol
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-6-methyl-1-phenol
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,6-dimethylphenol
 2,6-di(4''-tert. amyl-3'-phenoxybenzoylamino)-1-phenol
 2- α -(4'-tert. amylphenoxy)butyrylamino-1-phenol
 2-(α -acetamido- β -phenylethyl)-1-hydroxynaphthamide
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
 2-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-5-methyl-1-phenol
 2'-4''-tert. amyl-3'-phenoxybenzoylamino)-4-chloro-1-phenol
 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-6-chlorophenol
 3-(4''-tert. amyl-3'-phenoxybenzoylamino)phenol
 2-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-6-chlorophenol
 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-4-chlorophenol
 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-5-chlorophenol
 3-[α -(4'-tert. amylphenoxy)-n-butyrylamino]-2-chlorophenol
 2- α -(4'-tert. amylphenoxybutyrylamino)-5-chlorophenol
 2-(4''-tert. amyl-3'-phenoxybenzoylamino)-3-chlorophenol
 5-benzene sulfonamino-1-naphthol
 2,4-dichloro-5-benzenesulfonamino-1-naphthol
 2,4-dichloro-5-(p-toluenesulfonamino)-1-naphthol
 5-(1,2,3,4-tetrahydronaphthalene-6-sulfamino)-1-naphthol
 2,4-dichloro-5-(4'-bromodiphenyl-4-sulfonamino)-1-naphthol
 5-(quinoline-5-sulfamino)-1-naphthol

Any of the acylaminophenol couplers disclosed in Salminen and Weissberger U.S. Patent 2,423,730, dated July 8, 1947, can be used as couplers for the cyan image, e.g.



etc.

Couplers producing magenta images

1-p-sec. amylphenyl-3-n-amyl-5-pyrazolone
 2-cyanoacetyl-5-(p-sec. amylbenzoylamino)coumarone

2-cyanoacetylcoumarone-5-(n-amyl-p-sec. amyl-sulfanilide)
 2-cyanoacetylcoumarone-5-(N-n-amyl-p-tert. amyl-sulfanilide)
 5 2-cyanoacetylcoumarone-5-sulfon-N-n-butylanilide
 2-cyanoacetyl-5-benzoylamino-coumarone
 2-cyanoacetylcoumarone-5-sulfondimethylamide
 2-cyanoacetylcoumarone-5-sulfon-N-methylanilide
 2-cyanoacetylnaphthalene sulfon-N-methylanilide
 10 2-cyanoacetylcoumarone-5-(N- γ -phenylpropyl)-p-tert. amylsulfonamide
 1-p-laurylphenyl-3-methyl-5-pyrazolone
 1- β -naphthyl-3-amyl-5-pyrazolone
 1-p-nitrophenyl-3-n-amyl-5-pyrazolone
 15 1-p-phenoxyphenyl-3-n-amyl-5-pyrazolone
 1-phenyl-3-n-amyl-5-pyrazolone
 1,4-phenylene bis-3-(1-phenyl-5-pyrazolone)
 1-phenyl-3-acetyl-amino-5-pyrazolone
 1-phenyl-3-propionylamino-5-pyrazolone
 20 1-phenyl-3-n-valeryl-amino-5-pyrazolone
 1-phenyl-3-chloroacetyl-amino-5-pyrazolone
 1-phenyl-3-dichloroacetyl-amino-5-pyrazolone
 1-phenyl-3-benzoylamino-5-pyrazolone
 1-phenyl-3-(m-aminobenzoyl)-amino-5-pyrazolone
 25 1-phenyl-3-(p-sec. amylbenzoylamino)-5-pyrazolone
 1-phenyl-3-diamylbenzoylamino-5-pyrazolone
 1-phenyl-3- β -naphthoylamino-5-pyrazolone
 1-phenyl-3-phenylcarbonylamino-5-pyrazolone
 1-phenyl-3-palmitylamino-5-pyrazolone
 30 1-phenyl-3-benzenesulfonylamino-5-pyrazolone
 1-(p-phenoxyphenyl)-3-(p-tert. amyoxybenzoyl)-amino-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-benzamido-5-pyrazolone
 1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone
 35 1-(2',4',6'-trichlorophenyl)-3-phenylacetamido-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-phenylacetamido-5-pyrazolone
 1-(2',4'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amyl-phenoxyacetamido)benzamido]-5-pyrazolone
 1-(2',4',6'-trichlorophenyl)-3-[3''-(2''',4'''-di-tert. amyl-phenoxyacetamido)benzamido]-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-[3''-(2''',4'''-di-tert. amyl-phenoxyacetamido)benzamido]-5-pyrazolone
 40 1-(2',4',6'-trichlorophenyl)-3-[β -(2''',4'''-di-tert. amyl-phenoxy)-propionamido]-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-[β -(2''',4'''-di-tert. amyl-phenoxy)-propionamido]-5-pyrazolone
 1-(2',5'-dichloro)-3-[3''-(4'''-tert. amylphenoxy)benzamido]-5-pyrazolone
 50 1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert. amyl-phenoxy)-benzamido]-5-pyrazolone
 1-(2',5'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amyl-phenoxyacetamido)benzamido]-5-pyrazolone
 55 1-(2',4',6'-trichlorophenyl)-3-[α -(4-nitrophenoxy)acetamido]-5-pyrazolone
 1-(2',4',6'-trichlorophenyl)-3-(4-nitroanilino)-5-pyrazolone

Couplers producing yellow images

N-amyl-p-benzoylacetaminobenzenesulfonate
 N-(4-anisoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
 65 N-(4-benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
 N-(4-benzoylacetaminobenzenesulfonyl)-N-n-amyl-p-toluidine
 N-(4-benzoylacetaminobenzenesulfonyl)-N-benzyl-aniline
 70 ω -(p-Benzoylbenzoyl)acetanilide
 ω -Benzoylacet-2,5-dichloroanilide
 ω -Benzoyl-p-sec. amylacetanilide
 N,N'-di(ω -benzoylacetetyl)-p-phenylenediamine
 75 N,N'-di(acetoacetamino)diphenyl

α -{3-[α -(2,4-di-tert.-amylphenoxy)butyramido]benzoyl}-
2-methoxyacetanilide
 α -{3-[α -(2,4-di-tert.-amylphenoxy)acetamido]benzoyl}-
2-methoxyacetanilide
 4,4'-di-(acetoacetamino)-3,3'-dimethyldiphenyl
 p,p'-di-(acetoacetamino)diphenylmethane
 Ethyl-p-benzoylacetaminobenzenesulfonate
 Nonyl-p-benzoylacetaminobenzenesulfonate
 N-phenyl-N'-(p-acetoacetaminophenyl)urea
 n-Propyl-p-benzoylacetaminobenzenesulfonate acetoacet-
 piperidine
 ω -Benzoylacetpiperidine
 N(ω -benzoylactyl)-1,2,3,4-tetrahydroquinoline
 N(ω -benzoylactyl)morpholine

In addition to the above couplers, couplers which are particularly useful in color developers include couplers 1-64 listed in columns 3-5 of Spath U.S. Patent 2,956,876, issued October 18, 1960.

When the carbohydrazide of my invention is used in the form of an acid-addition salt, it is preferable to employ a buffering agent, such as sodium citrate, sodium acetate, sodium tetraphosphate, etc., inasmuch as some of the acid-addition salts of carbohydrazide have a tendency to have a rather low pH in aqueous solution. Such buffered solutions are substantially neutral, i.e., have a pH of about 7 (± 1.0 pH units). No buffer is needed, however, when carbohydrazide base is employed. Suitable acid-addition salts include those of acids, such as hydrochloric, hydrobromic, acetic, etc.

The carbohydrazide solutions used in my invention can vary in concentration, depending upon the hardness of the photographic layers undergoing treatment, the thickness of the layers, etc. In general, it has been found that the most useful treating solutions contain from about 2 to about 20 percent by weight of carbohydrazide. A particularly useful range comprises from about 5 to 10 percent by weight of the carbohydrazide. The concentration of the carbohydrazide will also depend somewhat upon the porosity of the photographic support, since porous supports, such as paper, will retain larger amounts of treating solutions than hydrophobic supports, such as film.

The temperature at which the treatments are carried out is not critical. As a matter of convenience, it may be desired to employ the treating solutions at room temperature. It is, of course, important that the temperature of the treating solutions should not be high enough to damage the photographic layer or element being treated, or to decompose or otherwise adversely effect the treating agent.

The treating time required in the present invention varies with the permeability to the treating solution of the photographic elements being treated. In general, a few minutes immersion in, or contact with (e.g., spraying, etc.), the treating bath is sufficient in most cases, although shorter or longer times may often be employed with success. It is, of course, essential that the photographic element be immersed long enough to absorb sufficient treating agent to provide a significant improvement in the stability of the color element against discoloration.

The invention will now be described more specifically in the following example which has been selected for purposes of illustration only and is not to be construed as limiting the scope of the invention.

EXAMPLE

A multi-layer photographic element of the type described in Mannes et al. U.S. Patent 2,252,718, issued August 19, 1941, was exposed to an original multi-colored scene and developed for about 3½ minutes at 80° F. in a developer having the following composition:

Quadrafos¹ -----g-- 0.6
 Sodium sulfite -----g-- 12.0
 p-N-methylaminophenol sulfate -----g-- 5.0

Sodium hydroxide -----g-- 1.0
 Hydroquinone -----g-- 2.0
 Sodium sulfite -----g-- 6.0
 Sodium carbonate -----g-- 35.0
 5 Potassium iodide (0.1% solution) -----ml-- 10.0
 Sodium bromide -----g-- 3.0
 Sodium thiocyanate -----g-- 1.75
 Water to one liter.

¹ Sodium tetraphosphate (or hexametaphosphate).

10 The photographic element was then spray washed with water for about ½ minute and given an exposure to red illumination of 1100 ft. candle seconds. The exposed material was then developed in a cyan developer having the following formula:

15 Carbohydrazide -----g-- 3.2
 Quadrafos¹ -----g-- 0.7
 Sodium bromide -----g-- 2.50
 Potassium iodide (0.1% solution) -----ml-- 5.0
 20 Sodium sulfite -----g-- 10.0
 Sodium sulfate -----g-- 20.0
 Sodium hydroxide -----g-- 3.30
 6-nitrobenzimidazole (1% solution, 1% sodium hydroxide) -----ml-- 5.0
 25 p-N-benzylaminophenol² -----g-- 0.70
 Coupler³ -----g-- 1.50
 4-amino-N,N-diethyl-3-methylaniline hydrochloride -----g-- 2.60
 Water to one liter.

¹ Sodium tetraphosphate.

² As hydrochloride.

³ 2-(o-acetamido- β -phenylethyl)-1-hydroxynaphthamide.

In place of the carbohydrazide, it was also found possible to use 4.7 g./liter of semicarbazide, 0.25 g./liter of hydroxylamine sulfate or 0.25 g./liter of hydrazine sulfate.

35 The photographic element was then washed for about ½ minute with water and exposed to blue light of 300 ft. candle seconds intensity and developed in a yellow color developer containing a phenylenediamine color-developing agent, such as 4-amino-N,N-diethylaniline hydrochloride and a yellow coupler, such as coupler No. 47 from column 4 of U.S. Patent 2,956,876. The photographic element was then washed and fogged chemically by treatment with a sodium borohydride solution, as described in Henn et al. U.S. Patent 2,984,567, issued May 16, 1961. The photographic element was then developed in a magenta color developer containing a color developing agent, such as 4-amino-N,N-diethyl-3-methylaniline hydrochloride and a magenta coupler, such as coupler No. 30 in column 4 of U.S. Patent 2,956,876.

45 The photographic element, processed as described above, was split into three pieces, one of which received no further treatment and served as a control. One of the remaining pieces was immersed in a 5% aqueous solution of urea for 10 minutes, while the remaining strip was immersed for the same period of time in a 5% aqueous solution of carbohydrazide. The strips were then removed from the solutions, dipped once in wash water and allowed to dry. The two treated strips and the strip serving as a control were then exposed to 300,000 foot-candle-hours of tungsten illumination and the density loss for the red, green and blue layers compared before and after treatment. The following table shows the density loss for each of the three strips where the original densities had been 1.0.

Addenda	Red D Loss	Green D Loss	Blue D Loss
70 Control-----	-.02	-.46	-.26
5% carbohydrazide-----	-.03	-.20	-.23
5% urea-----	-.02	-.43	-.27

75 Under comparable conditions, it can be seen from the above data that carbohydrazide had properties substan-

tially superior to urea in stabilizing the dye in the green or magenta layer.

In a manner similar to that illustrated above, color prints of the kind referred to in "Principles of Color Photography" by Evans, Hanson and Brewer, 1953, page 307, can be stabilized effectively using the carbonylhydrazide of my invention. Such color prints utilize three layers of light-sensitive silver halide emulsions containing prior to color development, respectively, color couplers for producing yellow, magenta and cyan dyes, the emulsions being coated on a paper support. After treatment, the prints can be squeezed and dried to yield treated material of outstanding stability.

As indicated above, a buffering agent can be added to the treating solution, especially where an acid-addition salt of the carbonylhydrazide is employed. Metal sequestering agents, such as ethylenediamine tetracetic acid tetrasodium salt can be added to eliminate iron staining.

As shown in the above example, the processed photographic elements should be treated after complete photographic processing with the treating solutions of the present invention in order that a significant quantity of the carbonylhydrazide remains in the finished photographic color element. The optional rapid water washing of the material treated according to the invention should be carried out in such a way that only surplus treating agent is removed from the surface of the element and no substantial amount of carbonylhydrazide is removed from the photographic layers containing the coupled dye images. If the carbonylhydrazide is merely included in the conventional photographic processing, such as developer, etc., it is obvious that it will be completely removed from the photographic element and the processed image will not have desirable stability.

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.

What I claim as my invention and desire secured by Letters Patent of the United States is:

1. A method of inhibiting discoloration in a photographic element which has been exposed, processed to a photographic record comprising at least one dye image

and in which residual silver and silver salts have been removed from said element, which comprises dispersing in the dye image areas of said photographic element an aqueous solution comprising carbonylhydrazide and drying said photographic element without substantial removal of said carbonylhydrazide.

2. A method of stabilizing a photographic element which has been processed to a photographic dye image by a reversal processing technique wherein the color-forming components are incorporated within a photographic color developer, and in which residual silver and silver halide are removed from said element, comprising dispersing throughout the dye image areas of said processed photographic element an aqueous solution comprising carbonylhydrazide and drying said photographic element without substantial removal of said carbonylhydrazide.

3. A method as defined in claim 2 wherein said photographic dye image comprises a dye selected from the class consisting of azomethine dyes, indoaniline dyes, indophenol dyes and indamine dyes.

4. A process according to claim 3 wherein said carbonylhydrazide is employed in a buffered solution in the form of an acid-addition salt.

5. A photographic color element which has been exposed, processed to a photographic record comprising a layer containing at least one dye image and in which residual silver and silver salts have been removed from said element, said element having been stabilized by the method of claim 1.

References Cited by the Examiner

UNITED STATES PATENTS

2,245,236	6/41	Trivelli et al. -----	96—109
2,311,098	2/43	Swan et al. -----	96—109
2,487,446	11/49	Kellog -----	96—56
2,772,973	12/56	Britain -----	96—55
2,788,274	4/57	Ranger -----	96—56
2,875,049	2/59	Kridel -----	96—59

OTHER REFERENCES

Glaflkides: Photographic Chemistry, vol. 2, 1960, Fountain Press London, p. 706.

45 NORMAN G. TORCHIN, *Primary Examiner.*