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STAIN PREVENTING SHORTSTOP BATH FOR PHOTOGRAPHIC AZINE DYE IMAGES

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6 Claims. (Cl. 95—88)

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This invention relates to photographic shortstop baths for removing color developer stains from phenazonium (azine) dyestuff images following color forming development with 2,4-diamino-aniline developing agents.

There is described in United States Patent 2,486,440, issued November 1, 1949, a method of producing azine dyestuff images by color developing silver halide emulsions with a 2,4-diamino-aniline in the presence of a color former.

The azine dyes produced in this way have unusual stability and superior spectral characteristics, particularly when compared with the quinonimine or azomethine dyes produced with developers of the p-phenylenediamine type.

Despite the many recognized advantages of this new class of color developers, they possess one disadvantage which provides a somewhat serious problem in the use of the azine method. This disadvantage occurs in the developement of multilayer film and is manifested, especially when the aromatic triamino developing solution is old and badly oxidized by leaving a developer stain in the processed film. This stain, in most cases, is quite substantive to gelatin and can usually be completely removed only by excessively long wash times after color development. This developer stain may be observed particularly in the highlights or whites of the processed film. In the color developed areas of the film, it produces a serious loss in color rendition. Furthermore, such a stain may contribute in no small degree to the loss of storage stability of the final color image, including both the so-called light and dark fading characteristics.

The stain originating from oxidation of the developer substance either in the solid state or in solution is not to be confused with stain that may be formed imagewise during the color development. In the former case, the developer substance is oxidized by air, probably to some sort of a dye, and this dye is adsorbed to the gelatin in a more or less random, over-all pattern. In the latter case, oxidized developer of a species different than that originating from aerial oxidation is formed by reduction of the "positive" silver halide image by the color developer. This transient oxidized developer form has recourse to at least two of several reactions: (1) to couple with a color former to produce an azine dye, or (2) to

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couple with another molecule of oxidized developer to produce a stain. In the case of stain arising from aerial oxidation of the developer, it was found that it could be removed almost completely if the film were washed sufficiently after color development. On the other hand, stain produced in situ during the color development step cannot be removed or destroyed any more than the dyes themselves may be removed or destroyed. Stain produced by aerial oxidation of the developer is a function of the general type of developing agent being used, whereas stain produced during color development is a function of the particular type of a developer being used. This is best exemplified in the case of the N-substituted 2,4-diamino-anilines used in the formation of azine dyestuffs. The 2,4-diamino-anilines, as a general class, are oxidized quite readily by air since they contain an additional amino group to the two present in the already unstable diamino-benzene type developers used in the formation of azomethine dyestuffs. On the other hand, within this general class of azine dye forming color developers, there are particular developers which do not produce imagewise stain, and there are other developers which do produce stain in the color development step.

It is known that developing, washing, and fixing baths, containing pyruvic acid, its ammonium or alkali metal salt, have been suggested by the art for the elimination of color stain in photographic silver halide emulsion layers containing quinonimine or azomethine dye images obtained by color forming development with primary aromatic amino developing agents. The pH of the treating bath must be alkaline or at least above the pH of 5, otherwise the azomethine link in the dyestuff image is cleaved. In other words, the azomethine dye image is discharged when the pyruvic acid treating bath is acid, i. e., of a pH of 2 to 4. In order to be effective, the pyruvic acid treating bath must contain a buffering agent to reduce the acidity and raise the pH from 5 to at least 8.

When a pyruvic acid shortstop bath of a pH of 5 to 8 is employed in the processing of multicolor film by the azine method while using 2,4-diamino-anilines for color development, the stain arising from aerial oxidation of the color developer is not diminished or eliminated.

Shortstop baths consisting of aqueous solutions of mineral acids or short chain aliphatic mono-, di-, and tribasic acids are also ineffective since they precipitate the 2,4-diamino-aniline color developers and lead to a product of extremely poor color rendition.

It is an object of the present invention to provide a simple and economical method of eliminating color stain from phenazonium dyestuff images obtained by color forming development with 2,4-diamino-aniline developing agents.

Other objects and advantages will become apparent from the following description.

We have now found that stains arising from aerial oxidation of 2,4-diamino-aniline developing agents in the color forming development of azine dyestuff images are readily eliminated by treating a multilayer color film, after color forming development, with an aqueous shortstop bath containing from 0.5 to 5% of a pyruvic acid. Best results are obtained when the concentration of such acid is in the range of 3 to 5%.

The shortstop bath may be used with any N-substituted 2,4-diamino-aniline developer, especially those in which the nitrogen atom in the 2-position bears an aliphatically bound hydrophylic group. Developers of this type produce a minimum of imagewise stain formed during color development. The bath may be used after the color development of either a monolayer or a multilayer. It is equally effective as a shortstop after color development, whether it be the development of an emulsion containing a non-diffusing color former or the development by diffusion of a silver halide emulsion by a developer solution containing the color former. The bath is also equally effective after either reversal or negative color development.

When using the preferred concentration of 3 to 5%, the shortstop bath has a pH ranging from 2 to 4. At this pH, the pyruvic acid neutralizes the developing media and stops further development.

The most unusual feature of the present invention is that while the pyruvic acids neutralize the developing media and stop further development, they do not precipitate the 2,4-diamino-aniline developing agent as is the case with mineral and short chain aliphatic mono-, di-, and tribasic acids. It is believed that this unusual property is attributable to the pyruvic acids or their degradation product, such as acetaldehyde (formed by the loss of CO_2) which readily reacts with the 2,4-diamino-aniline developing agent or its reaction product to give a water soluble product.

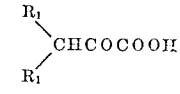
Any pyruvic acid may be used for our purpose, i. e., pyruvic acid itself, or α-substituted derivatives thereof. These compounds may be exemplified by the following general formula:

A—COCOOH

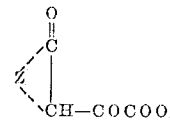
wherein the α-substituent represented by A is either an alkyl, e. g., methyl, ethyl, propyl, isopropyl, butyl, etc., mono- or di-(carboxy)methyl, alkylketomethyl, e. g., acetonyl, ethylketomethyl, butylketomethyl, etc., mono- or di-(acetyl)-methyl arylketomethyl, e. g., phenacyl, p-tolylketomethyl, m-xylketomethyl, etc., β-alkylethenyl, e. g., propenyl, isopropenyl, 1- or 2-methylpropenyl, 2-, or 3-butenyl, 3-methyl-1-butenyl, 1-pentenyl, etc., β-arylethenyl, e. g., styryl, methylstyryl, etc., or a 2-keto-saturated carbocyclic or N-heterocyclic radical having a 6-membered ring including at least 5 carbon atoms, e. g., 2-cyclohexanonyl, methyl-2-cyclohexanonyl, 3-(α-piperidonyl), etc.

The pyruvic acids may be further characterized by the following general formulae:

(1) $R—CH_2COCOOH$

(2) 

(3) $R_2=CHCOCOOH$

(4) 

wherein R represents either hydrogen or an alkyl group, e. g., methyl, ethyl, propyl, isopropyl, butyl, etc., or acyl group, e. g., acetyl, propionyl, butyryl, α-toluyl, o-, m-, or p-toluyl, cumoyl, etc., each of the R_1s represents either carboxy or acetyl, R_2 represents an alkylidene or arylidene group, e. g., ethylidene, propylidene, isopropylidene, butylidene, isobutylidene, benzylidene, p-methylbenzylidene, cinnamylidene, cuminylidene, etc., and Z represents the atoms necessary to complete a cyclohexanonyl or piperidinyl ring.

The following compounds are illustrative of the pyruvic acids contemplated by the present invention:

(1) $CH_3COCOOH$

Pyruvic acid

(2) $CH_3CH_2COCOOH$

3-methyl-pyruvic acid

(3) $CH_3COCH_2COCOOH$

Acetyl-pyruvic acid

(4) $C_6H_5COCH_2COCOOH$

Benzoyl-pyruvic acid

(5) $p\text{-}CH_3C_6H_5COCH_2COCOOH$

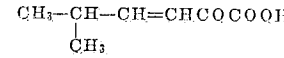
p-Toluyl-pyruvic acid

(6) $CH_3CH=CHCOCOOH$

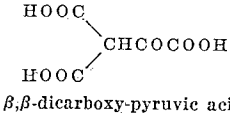
Methylmethinyl-pyruvic acid

(7) $C_6H_5CH=CHCOCOOH$

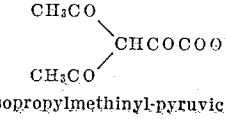
Phenylmethinyl-pyruvic acid

(8) 

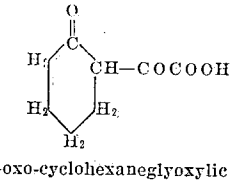
β,β-diacetyl-pyruvic acid

(9) 

β,β-dicarboxy-pyruvic acid

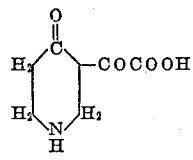
(10) 

Isopropylmethinyl-pyruvic acid

(11) 

2-oxo-cyclohexaneglyoxylic acid

(12)



4-oxo-3-piperidineglyoxylic acid

A shortstop bath employing any one of the pyruvic acids is prepared by simply dissolving the acid in water. If desired, a buffering agent, such as sodium sulfate or potassium alum, may be added in a concentration ranging from 10 to 60 grams per liter of shortstop bath to bring the bath to the specified pH and to maintain the pH even though small amounts of alkali may be carried into the bath by the color developed film.

The following compositions are illustrative of the shortstop baths with or without buffering agents which have a pH ranging from 2 to 4:

(1)	Pyruvic acid	grams	30
	Water to make	cc	1000
(2)	2-oxo-cyclohexaneglyoxylic acid	grams	10
	Water to make	cc	1000
(3)	Pyruvic acid	grams	50
	Potassium alum	do	15
	Water to make	cc	1000
(4)	β,β-dicarboxy-pyruvic acid	grams	35
	Water to make	cc	1000
(5)	Methylmethinyl-pyruvic acid	grams	25
	Sodium sulfate	do	60
	Water to make	cc	1000
(6)	Benzoyl-pyruvic acid	grams	15
	Water to make	cc	1000
(7)	Methyl-pyruvic acid	grams	30
	Potassium alum	do	10
	Water to make	cc	1000
(8)	β,β-diacetyl-pyruvic acid	grams	5
	Water to make	cc	1000

The 2,4-diamino-anilines which are utilized as the color developers for the production of azine dyestuff images are of the type described in the aforementioned Patent No. 2,486,440 and in application Serial No. 101,913, filed June 28, 1949, and entitled "Color Developers for the Production of Azine Dye Images."

Specific examples of such developing agents are:

4 - (β - hydroxyethylamino) - 6 - (4' - carboxymethoxy-phenylamino) -metanilic acid
4-(carboxymethylamino) -6-(4'-methoxy-phenylamino) -metanilic acid
2-(β-sulfoethylamino) -4-phenylamino aniline
4,6-di(β-hydroxyethylamino) -metanilic acid
4 - (β-hydroxyethylamino) - 6 - phenylamino-metanilic acid
2 - (β - hydroxyethylamino) - 4 - (β-sulfoethylamino) -5-methyl aniline
4-(β-hydroxy-β-methyl - ethylamino) -6-phenylamino-metanilic acid
4 - [α - di(hydroxyethyl) ethylamino] - 6 - (3'-ethoxy-phenylamino) -metanilic acid
4 - (β - hydroxyethylamino) - 6 - methylamino-metanilic acid
4 - (sulfomethylamino) -6-(methylphenylamino) -metanilic acid
4 - (β - hydroxyethylamino) - 6 - methylamino-metanilic acid

Color formers which are used with the aforementioned developers to give yellow azine dye images are also described in the aforementioned application Serial No. 101,913. These compounds are typified by the fact that they are open chain ketomethylene compounds. Examples of such compounds are:

Acetoacetanilide
N-1-naphthylacetoacetamide
N,N'-ethylenebisacetoacetamide
p,p'-Bi-o-acetoacetaniside
N-2-naphthaylbenzoylacetamide
p,p'-Bi-acetoacetanilide
α,α' - Terephthaloylbis-(3-chloro-4,6-dimethoxy-acetanilide)
α-Benzoylacetanilide

Preferably, the color formers utilized contain a group rendering them non-migratory in the emulsion. Examples of such compounds are:

2-(m-benzoylacetamidophenyl) - 1 - octadecyl-5-benzimidazolesulfonic acid
3,3' - ureylenebis - 5 - p - benzoylacetamidobenzamide-benzenesulfonic acid
2-p - benzoylacetamidobenzamido - 6 - stearoylamino-p-toluenesulfonic acid
2 - (p - benzoylacetamidophenyl) - 1 - octadecyl-5-benzimidazolesulfonic acid
p-Cyanoacetyl-3-octadecenylsuccinalic acid

Color formers capable of producing magenta dyestuff images are also described in the above-identified application as well as in application Serial No. 793,533, filed December 23, 1947, and entitled "Magenta Colored Phenazonium Dyestuff Images," now Patent No. 2,524,741, dated October 3, 1950. Preferably, these color formers are 6-halogen-8-hydroxy-quinolines, and particularly those which are non-migratory in the emulsions. Examples of the latter type compounds are:

6-stearoylamino- 2 -(2'-phenyl- 6'-bromo- 8' - hydroxy-cinchoninoyl) -aminotoluene- 4 -sulfonic acid
2 - phenyl- 6 -chloro- 8 -hydroxy-cinchoninoyl-octadecyl taurine
6 - decoxy - 3 - (2 - phenyl - 6 - bromo - 8 - hydroxy-cinchoninoyl) - amino-benzenesulfonic acid
2 - (3 - stearoylaminophenyl) - 6 - bromo - 8 - hydroxy-cinchoninic acid
2 - stearoylamino - 6 - (6 - chloro - 8 - hydroxy-cinchoninoyl) -aminotoluene - 4 - sulfonic acid, and the like.

Color formers for the cyan image are also described in application Serial No. 101,913, now Patent No. 2,570,116, dated October 2, 1951, and in United States Patent 2,445,252, issued July 13, 1948. Preferably, these color formers are aryl-J-acid derivatives, particularly those containing a group rendering the color former non-migratory in the emulsion. Examples of the latter compounds are:

Dodecyl urethane of β-sulfoethyl-J-acid
Tetradecyl urethane of p-anisyl-J-acid
2-hexadecyl urethane of phenyl-J-acid
4-stearoylaminophenyl-J-acid, and the like

The following examples serve to illustrate the invention, but it is to be understood that the invention is not restricted thereto.

Example I

A photographic silver bromide emulsion was exposed, the latent image developed in a black and white developer, re-exposed, and the residual

silver halide developed for 10 minutes in a solution of the following composition:

Sodium carbonate, monohydrate	grams	40
Sodium sulfite	do	40
Ethylenediamine	do	15
8-Hydroxyquinoline	do	3
4-(β-hydroxyethylamino)-6-phenylamino-metanilic acid	do	5
Water to make	cc	1000

After development, the film was rinsed and treated for 3 minutes in a bath of the following composition:

3-(2-cyclohexanonyl)-pyruvic acid	grams	30
Water to make	cc	1000

The film was then washed, bleached in ferricyanide bleach and fixed in an acid hardening hypo solution. There is thus obtained a brilliant magenta azine dyestuff free from stain.

Example II

An integral tripack with a bottom layer composed of a red-sensitive emulsion containing phenyl-J-acid-N-octadecyl urethane; a middle layer composed of a green-sensitive emulsion containing 2-stearoylamino-6-(8-hydroxycinchoninoylamino)-toluene-4-sulfonic acid, and a top layer composed of a blue-sensitive emulsion containing 2-(4-benzoylacetaminophenyl)-1-octadecyl-5-benzimidazolesulfonic acid was exposed and the latent image developed in a black and white developer, re-exposed, and the residual silver halide developed in a solution of the following composition:

Sodium carbonate, monohydrate	grams	40
Sodium sulfite	do	60
Potassium bromide	do	5
Pyridine	do	16
Benzylamine	do	1
4-(β-hydroxyethylamino)-6-phenylamino-metanilic acid	do	5
Water to make	cc	1000

After color development, the film was rinsed and treated for 5 minutes in a bath of the following composition:

Pyruvic acid	grams	50
Potassium alum	do	15
Water to make	cc	1000

The film was washed, bleached in a ferricyanide bleach and fixed in an acid hardening solution. There was obtained a multicolor, stain-free positive dye image.

Example III

An integral tripack of essentially the same composition as used in Example II was exposed and color developed for 15 minutes to a negative image in a solution of the following composition:

Trisodium phosphate	grams	40
Sodium sulfite	do	40
Potassium bromide	do	12.5
Hydroxylamino hydrochloride	do	1
4-(β-hydroxyethylamino)-6-benzylamino-metanilic acid	do	6
Water to make	cc	1000

After development, the film was rinsed and treated for 5 minutes in a bath of the following composition:

Methylmethinyl-pyruvic acid	grams	40
Sodium sulfate	do	50
Water to make	cc	1000

The film was washed, bleached in ferricyanide bleach, and fixed in an acid hardening hypo. There was obtained a brilliant, multicolor negative dye image, completely free from stain.

We claim:

1. In the process of producing subtractivly colored azine dye images in a silver halide emulsion layer containing a color former capable of coupling with the oxidation products of a 2,4 diaminoaniline developing agent to form an azine dye which comprises exposing the emulsion and developing the same with a color developer containing as the effective developing agent a 2,4-diamino-aniline, the improvement which comprises avoiding the formation of stain after the color development by shortstopping the color developed emulsion with an aqueous bath having a pH ranging from 2 to 4 and containing an organic acid of the class consisting of pyruvic acid and its β-acyl, β-alkyl, β-aryl, and β-carboxy-substituted derivatives.

2. In a process according to claim 1, wherein the acid is pyruvic acid.

3. In a process according to claim 1, wherein the acid is 2-oxo-cyclohexaneglyoxylic acid.

4. In a process according to claim 1, wherein the acid is methylmethinyl-pyruvic acid.

5. In a process according to claim 1, wherein the acid is methyl-pyruvic acid.

6. In a process according to claim 1, wherein the acid is β,β-dicarboxy-pyruvic acid.

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