

1

3,128,182

SILVER HALIDE SOLVENT CONTAINING DEVELOPERS AND PROCESS

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No Drawing. Filed Oct. 23, 1961, Ser. No. 147,055
20 Claims. (Cl. 96-61)

This invention relates to photography, and more particularly, to photographic developers for use in reversal processing of photographic color films and papers.

In multi-layer photographic elements used for color photography, there are usually at least three selectively sensitive emulsion layers coated on a conventional photographic support, such as cellulose ester film, paper, polyvinyl resin film, polyester film, etc. For example, the uppermost silver halide emulsion layer may be blue-sensitive, while the silver halide emulsion layer closest to the support may be red-sensitized. Between these two emulsion layers, there may be a green sensitized silver halide emulsion layer. Frequently, a yellow filter layer is used between the blue-sensitive and the green-sensitized silver halide emulsion layer. Of course, additional silver halide emulsion layers, gelatin interlayers, and the like, may also be present. The silver halide emulsion layers may contain some of the processing ingredients, such as the color-forming compounds or couplers. In processing multi-layer color materials of the type useful in our invention, the photographic material is first processed to a conventional black-and-white silver negative in a developer which does not contain a developing agent capable of coupling with any of the color-forming compounds or couplers which may be present. Without removing unexposed silver halide, the material is given a reversal exposure, followed by color development. The technique of color reversal processing is well known to those skilled in the photographic art and color materials which can be used in such processing have been previously described in a number of domestic and foreign patents, such as Mannes et al. U.S. Patent 2,252,718, issued August 19, 1941.

The color materials useful in the present invention include those having silver halide emulsion layers containing the color-forming materials or couplers in a layer, or layers, as well as color materials intended for processing in a color developer which contains the color coupler.

It is, therefore, an object of our invention to provide improved developers for reversal color photography. Another object is to provide a method of processing reversal color materials using the improved developers of our invention. Other objects will become apparent from a consideration of the following description and examples. In the processing of various photographic materials, it has been rather common to employ silver halide solvents in the photographic silver halide developing compositions for the purpose of accelerating either black-and-white or color development. However, some of the amines which have been previously used in the developing compositions of photographic color materials have been found to be highly toxic and quite volatile. In addition, some of these amines readily form carbamates in the photographic developers commonly used and some of

2

them have the added disadvantage of reducing the definition of the colored images formed in certain of the sensitized layers, particularly the green-sensitized layer which develops into a magenta image. Some of these amines also interfere with development so that development does not proceed to the production of an image of desired density.

While some amines have useful properties for specific types of photographic developers, such properties are usually unique and limited to the use of a particular set of conditions. These amine silver halide solvents when used in the black-and-white developers will affect the curve shapes of all sensitized layers as well as affecting the overall speed and fog, while in a color developer, the curve shape of the layer being developed is primarily affected, as well as the covering power of the resulting dye, silver/dye ratio, and the sharpness of the dye image. The activity of certain of the silver halide solvents, such as isopropylamine, particularly in the black-and-white developer, is lower where the alkaline material is an alkali metal carbonate, since such silver halide solvents readily form carbamates with the carbonate, resulting in a serious loss of the silver halide solvent.

We have now found that the afore-mentioned difficulties in the black-and-white developing solutions, as well as the color developing solutions, can be entirely or largely overcome by using as silver halide solvents, cyclohexane compounds containing an amino radical, and in addition to the amino radical, a polar substituent, such as hydroxyl, amino, hydroxyalkyl (hydroxyethyl, hydroxypropyl, etc.), etc. Particularly useful cyclohexane compounds are those which contain an aminomethyl substituent. Typical cyclohexane compounds useful in our invention comprise 1,4-bis(methylamino)cyclohexane, 4-aminocyclohexanol, 1-cyclohexaneamino-2-propanol, etc.

It has been found that the cyclohexane compounds of our invention, when used either in the black-and-white negative developer, or in one or more of the color developers, have adequate photographic activity and permit reasonable film speeds with very low fog density. They have low volatility, low toxicity, high water solubility and only a slight tendency to form carbamates under the alkaline conditions present in many of these photographic developers. In addition, when these cyclohexane compounds are employed in color developers, they show no tendency to reduce the sharpness of the color images.

The cyclohexane compounds used as silver halide solvents in our invention can be employed under rather wide concentration ranges, depending upon the type of silver halide developer, concentration of alkali, type of alkali, type of coupler, etc. In general, we have found that quite useful results are obtained in black-and-white silver halide negative developers if the concentration of the cyclohexane compound varies from about 0.5 to 10 grams per liter. Approximately the same concentration ranges for the cyclohexane compound can be employed in color developers, although we have found that especially good results are obtained within the range of about 1 to 8 grams per liter.

The cyclohexane compounds of our invention can be employed in a variety of aqueous alkaline solutions containing various photographic developing agents. The black-and-white negative developing agents which have

been found particularly useful in our invention comprise the dihydroxybenzenes, such as hydroquinone, toluquinone, etc., N-methyl-p-aminophenol salts, etc., or mixtures of such developing agents. Also, useful in the negative developers of our invention are the 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, etc.

Any of the conventional color-forming developing agents which have been previously described in the prior art can be used in our invention. The color-forming developers or developing agents which have been found to be especially useful in our invention include aromatic primary amines containing an amino (substituted or not) or hydroxyl substituent. Phenylenediamines and substituted derivatives thereof containing a primary amino group are especially useful in our invention. Typical of color-forming developers are the sulfonamido substituted p-phenylenediamines disclosed in Weissberger et al., U.S. Patent 2,548,574, issued April 10, 1951; the substituted p-phenylenediamines disclosed in Weissberger et al., U.S. Patent 2,566,271, issued August 28, 1951, etc.

The pH of the developers useful in our process, including both the color developers and the black-and-white negative developers, can vary depending upon the particular photographic material which is to be processed in the developers. In the case of color developers, it has been found that the cyclohexane compounds of our invention are outstanding at relatively high pH values, i.e., where the pH is at least 10.0 and as high as 11.5 to 12.5.

Our invention is primarily directed to the development of the ordinarily employed gelatino-silver-halide developing-out emulsions, e.g., gelatino-silver-chloride, -chlorobromide, -chloriodide, -chlorobromiodide, -bromide, -bromiodide, etc. While the results illustrated below were obtained using gelatino-silver bromiodide emulsions, excellent results can be obtained using other silver halide emulsions. These emulsions can be coated in the usual manner on a suitable support, e.g., glass, cellulose nitrate film, cellulose acetate film, polyvinyl film, polyester film, paper, metal, etc.

Photographic silver halide emulsions useful in our invention can also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allyl thiocarbamide, thiourea, allyl isothiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.) (see U.S. Patents 2,540,085; 2,597,856 and 2,597,915), various azaindene compounds (such as those disclosed in U.S. Patent 2,716,062), condensation products of alkylene oxides, such as those shown in U.S. Patent 2,400,532, as well as the additives mentioned in Jones et al., U.S. Patent 2,937,089.

Typical color-forming compounds or couplers which are useful in color photography, according to our invention, include the following:

COUPLERS PRODUCING CYAN IMAGES

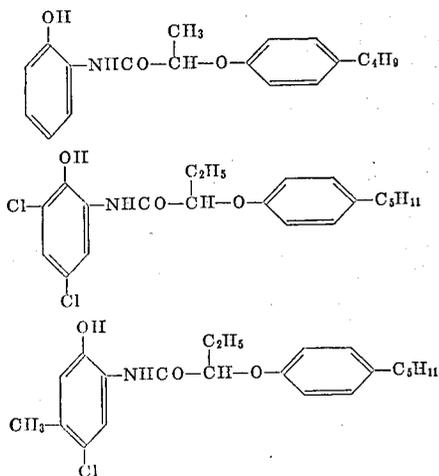
5-(p-amyphenoxybenzenesulfonamino)-1-naphthol
5-(N-benzyl-N-naphthalenesulfonamino)-1-naphthol
5-(n-benzyl-N-n-valeryl-amino)-1-naphthol
5-caproylamino-1-naphthol
2-chloro-5-(N-n-valeryl-N-p-isopropylbenzylamino)-1-naphthol
2,4-dichloro-5-(p-nitrobenzoyl-β-o-hydroxyethylamino)-1-naphthol
2,4-dichloro-5-palmitylamino-1-naphthol
2,2'-dihydroxy-5,5'-dibromostilbene
5-diphenylethersulfonamido-1-naphthol
1-hydroxy-2-(N-isoamyl-1-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-phenylpropionyl-p-sec-amyphenylamino)-1-naphthol

- 5 2-acetylamino-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]phenoxyacetamido-2,4-dichloro-3,5-dimethylphenol
- 10 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
- 15 2-(4''-tert. amy-3'-phenoxybenzoyl)-amino-3,5-dimethyl-1-phenol
2-phenylacetylamino-4-chloro-5-methylphenol
2-benzoylamino-4-chloro-5-methylphenol
- 20 2-anilinoacetylamino-4-chloro-5-methylphenol
2-{4'-[α-(4''-tert. amyphenoxy)-n-butyrylamino]-p-tylamino}-4-chloro-5-methylphenol
2-[4',3''-(4'''-tert. amyphenoxy)benzoylamino]benzoylamino-4-chloro-5-methylphenol
- 25 2-p-nitrobenzoylamino-4-chloro-5-methylphenol
2-m-aminobenzoyl-4-chloro-5-methylphenol
2-acetamino-4-chloro-5-methylphenol
2(4'-sec. amybenzylamino)-4-chloro-5-methylphenol
2(4'-n-amyloxybenzylamino)-4-chloro-5-methylphenol
- 30 2(4'-phenoxybenzoylamino)phenol
2(4''-tert. amy-3'-phenoxybenzoylamino)phenol
2-[α-(4'-tert. butylphenoxy)propionylamino]phenol
2-[α-(4'-tert. amy)phenoxypropionylamino]phenol
2-[N-methyl-N-(4''-tert. amy-3'-phenoxybenzoylamino)]phenol
- 35 2-(4''-tert. amy-3'-phenoxybenzoylamino)-3-methyl-1-phenol
2-(4''-tert. amy-3'-phenoxybenzoylamino)-6-methyl-1-phenol
- 40 2-(4''-tert. amy-3'-phenoxybenzoylamino)-3,6-dimethyl-1-phenol
2,6-di(4''-tert. amy-3'-phenoxybenzoylamino)-1-phenol
2-α-(4'-tert. amyphenoxy)butyrylamino-1-phenol
- 45 2-(o-acetamido-β-phenylethyl)-1-hydroxynaphthamide
2(4''-tert. amy-3'-phenoxybenzoylamino)-3,5-dimethyl-1-phenol
2-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-5-methyl-1-phenol
- 50 2(4''-tert. amy-3'-phenoxybenzoylamino)-4-chloro-1-phenol
3-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-6-chlorophenol
3-(4''-tert. amy-3'-phenoxybenzoylamino)phenol
- 55 2-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-6-chlorophenol
3-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-4-chlorophenol
3-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-5-chlorophenol
3-[α-(4'-tert. amyphenoxy)-n-butyrylamino]-2-chlorophenol
- 60 2-α-(4'-tert. amyphenoxy)butyrylamino]-5-chlorophenol
2-(4''-tert. amy-3'-phenoxybenzoylamino)-3-chlorophenol
5-benzene sulfonamino-1-naphthol
2,4-dichloro-5-benzenesulfonamino-1-naphthol
2,4-dichloro-5-(p-toluenesulfonamino)-1-naphthol
- 70 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
- 75 Any of the acylaminophenol couplers disclosed in Sal-

5

minen 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-cyanoacetyl coumarone-5-(n-amyl-p-sec. amylsulfanilide)
 2-cyanoacetyl coumarone-5-(N-n-amyl-p-tert. amylsulfanilide)
 2-cyanoacetyl coumarone-5-sulfon-N-n-butylanilide
 2-cyanoacetyl-5-benzoylamino coumarone
 2-cyanoacetyl coumarone-5-sulfondimethylamide
 2-cyanoacetyl coumarone-5-sulfon-N-methylanilide
 2-cyanoacetyl naphthalene sulfon-N-methylanilide
 2-cyanoacetyl coumarone-5-(N-γ-phenylpropyl)-p-tert. amylsulfonilide
 1-p-laurylphenyl-3-methyl-5-pyrazolone
 1-β-naphthyl-3-amyl-5-pyrazolone
 1-p-nitrophenyl-3-n-amyl-5-pyrazolone
 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-propionyl amino-5-pyrazolone
 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
 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-palmityl amino-5-pyrazolone
 1-phenyl-3-benzenesulfonylamino-5-pyrazolone
 1-(p-phenoxyphenyl)-3-(p-tert. amyloxybenzoyl) amino-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-benzamido-5-pyrazolone
 1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone
 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. 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-[β-(2''',4'''-di-tert. amylphenoxy)-propionamido]-5-pyrazolone

6

- 1-(2',5'-dichloro)-3-[3''-(4'''-tert. amylphenoxy) benzamido]-5-pyrazolone
 1-(2',4',6'-tribromophenyl)-3-[3''-(4'''-tert. amylphenoxy) benzamido]-5-pyrazolone
 1-(2',5'-dichlorophenyl)-3-[3''-(2''',4'''-di-tert. amylphenoxyacetamido) benzamido]-5-pyrazolone
 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
 N-(4-benzoylacetaminobenzenesulfonyl)-N-benzyl-m-toluidine
 N-(4-benzoylacetaminobenzenesulfonyl)-N-n-amyl-p-toluidine
 N-(4-benzoylacetaminobenzenesulfonyl)-N-benzylaniline
 ω-(p-Benzoylbenzoyl) acetanilide
 ω-Benzoylacet-2,5-dichloroanilide
 ω-Benzoyl-p-sec. amylacetanilide
 N,N'-di(ω-benzoylacetyl)-p-phenylenediamine
 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-benzoylacetyl)-1,2,3,4-tetrahydroquinoline
 N-(ω-benzoylacetyl) 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. Couplers which are useful in photographic silver halide emulsion layers include couplers 65-77 in column 5 of U.S. Patent 2,956,876. Other couplers suitable for use in the emulsions of our invention include those described in Spence and Carroll U.S. Patent 2,640,776, issued June 2, 1953; Weissberger et al. U.S. Patent 2,407,210, issued September 3, 1946, and Weissberger et al. U.S. Patent 2,474,293, issued June 28, 1959.

The following examples will serve to illustrate the manner of practicing our invention.

Example 1

- A portion of a gelatino-silver-bromide emulsion which had been sensitized with a sulfur compound and a gold salt as mentioned above, was coated on a cellulose acetate support and dried. The coating was then cut into several strips and one strip of each was then exposed for $\frac{1}{25}$ second to a 500-watt, 3000° K. light source on an Eastman Type Ib sensitometer. One of the exposed strips was then developed for 3 minutes in a developer having the following composition:
- | | | | |
|----|----------------------------------|-------|------|
| 55 | Sodium hexametaphosphate | g-- | 0.4 |
| | Sodium sulfite (anhydrous) | g-- | 40.0 |
| | N-methyl-p-aminophenolsulfate | g-- | 5.0 |
| | Hydroquinone | g-- | 2.0 |
| | Sodium carbonate (monohydrate) | g-- | 25.0 |
| 70 | Potassium bromide | g-- | 1.0 |
| | Potassium iodide (0.1% solution) | ccs-- | 2 |
| | Water to make one liter. | | |
| | (pH was 10.1 at 70° F.) | | |

- 75 The strip was then washed for about 2 minutes in water

7

and then given a reversal exposure for about 10 seconds (flash) with a No. 2 Photoflood set at a distance of about 60 inches. The strip was then developed for approximately 5 minutes in a developer having the following formula:

Sodium hexametaphosphate	g	1.0
Sodium sulfite (anhydrous)	g	30
Sodium sulfate	g	30
Sodium bromide	g	0.5
Potassium iodide (0.1% solution)	ccs	5
1,4-bis(aminomethyl)cyclohexane	g	5
Coupler ¹	g	0.85
Sodium hydroxide	g	3
Color developer ²	g	3
Hydroxylamine sulfate	g	0.35
Water to make 1 liter.		
(pH at 80° F. was 12.40.)		

¹ 1-(2',4',6'-trichlorophenyl)-3-[a-(4-nitrophenoxy)-acetamidol]-5-pyrazolone.

² 4-amino-N,N-diethyl-3-methylaniline hydrochloride.

The strip was then washed for about 10 minutes in water and treated for about 2 minutes in a silver bleach bath having the following composition:

Potassium ferricyanide	G.	100
Potassium bromide		10
Borax		7.5
Boric acid		5.0
Water to make 1 liter.		

The strip was then treated for about 2 minutes in a fixing bath having the following composition:

Sodium thiosulfate (pentahydrate)	G.	200
Sodium sulfite (anhydrous)		10
Water to make 1 liter.		

The strip was then washed in water and dried. The processed strip showed good definition and speed.

In order to show that the cyclohexane compounds of our invention are unique in photographic developers, one of the exposed strips was processed in a manner identical to that illustrated in the above example, except that the cyclohexane compound was omitted from the color developer. The strip processed in the color developer containing the cyclohexane compound had a D-max. difference of only $-.14$ compared to the control strip. On the other hand, when one of the exposed strips of Example 1 was processed as described in that example, except that cyclohexylamine was used in place of the 1,4-bis(methylamino)cyclohexane in the color developer, there was a magenta D-max. difference of $-.48$ compared to the control. These results can be summarized as follows.

Addenda—Color developer:	Δ D-max.	from control
Control		55
Cyclohexylamine		-.48
1,4-bis(methylamino)cyclohexane		-.14

Example 2

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:

Hydroquinone	g	2.5
N-methyl-p-aminophenol sulfate	g	4.5
4-aminocyclohexanol	g	6
Sodium sulfite (anhydrous)	g	80
Sodium carbonate H ₂ O	g	30
Sodium bromide	g	2.5
Sodium hexametaphosphate	g	0.5
Potassium iodide (0.1% solution)	ccs	15
Water to one liter.		
(pH 10.3.)		

8

The photographic element was then spray washed with water for about 30 seconds and exposed to red illumination of about 1100 ft. candle seconds. The exposed material was then developed in a cyan developer having the following formula:

Carbohydrazide	g	3.2
Quadrofos ¹	g	0.7
Sodium bromide	g	2.50
Potassium iodide (0.1% solution)	ml	5.0
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
p-N-benzylaminophenol ²	g	0.70
Coupler ³	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.

The photographic element was then washed for about 30 seconds with water and exposed to blue light of 300 ft. candle seconds intensity and developed in a yellow color-producing 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. The photographic element was then developed in a magenta color developer containing a color-developing agent, such as that used in Example 1 above and a magenta coupler, such as Coupler No. 30 in column 4 of U.S. Patent 2,956,876.

The photographic element was then bleached, fixed and dried as described in Example 1.

As compared with a photographic element which had been similarly processed using a negative developer containing 6.5 grams per liter of isopropylamine, it was noted that there was a substantial speed increase for the material processed in the 4-aminocyclohexanol (approximately ½ stop), that there was a relatively small loss in reversal D-max. (0.15 unit) and that there was an increase in the speed/fog ratio compared to the material processed in the developer containing the isopropylamine. In order to produce a material processed in a negative developer containing isopropylamine and provide a speed comparable to material processed in the 4-aminocyclohexanol-containing developer, it was found necessary to increase the isopropylamine concentration to such an extent that the D-max. of the resulting image was materially reduced in all layers of the elements.

Example 3

Example 2 was repeated using a negative developer containing 6.0 grams per liter of 1-cyclohexylamino-2-propanol in place of the 4-aminocyclohexanol used in Example 2. Again, there was a substantial increase in speed compared to material processed in a negative developer containing isopropylamine as the silver halide solvent.

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 we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic developing composition consisting of an aqueous alkaline solution comprising a photographic developing agent and a silver halide solvent comprising a cyclohexane containing an amino radical attached to the

carbocyclic ring thereof and in addition to said amino radical, a polar substituent selected from the class consisting of an amino radical, a hydroxyl radical and a hydroxyalkyl radical.

2. A photographic developing composition consisting of an aqueous alkaline solution comprising a photographic developing agent and 1,4-bis(methylamino)cyclohexane.

3. A photographic developing composition consisting of an aqueous alkaline solution comprising a photographic developing agent and 4-aminocyclohexanol.

4. A photographic developing composition consisting of an aqueous alkaline solution comprising a photographic developing agent and 1-cyclohexylamino-2-propanol.

5. A photographic developing composition consisting of an aqueous alkaline solution comprising at least one photographic developing agent selected from the class consisting of 3-pyrazolidones, dihydroxybenzenes and p-N-methylaminophenol salts, and a silver halide solvent comprising a cyclohexane containing an amino radical attached to the carbocyclic ring thereof and in addition to said amino radical, a polar substituent selected from the class consisting of an amino radical, a hydroxyl radical and a hydroxyalkyl radical.

6. A photographic developing composition consisting of an aqueous alkaline solution comprising at least one photographic silver halide developing agent selected from the class consisting of 3-pyrazolidones, dihydroxybenzenes and p-N-methylaminophenol salts, and 1,4-bis(methylamino)cyclohexane.

7. A photographic developing composition consisting of an aqueous alkaline solution comprising at least one photographic silver halide developing agent selected from the class consisting of 3-pyrazolidones, dihydroxybenzenes and p-N-methylaminophenol salts, and 4-aminocyclohexanol.

8. A photographic developing composition consisting of an aqueous alkaline solution comprising at least one photographic silver halide developing agent selected from the class consisting of 3-pyrazolidones, dihydroxybenzenes and p-N-methylaminophenol salts, and 1-cyclohexylamino-2-propanol.

9. A photographic developing composition consisting of an aqueous alkaline solution comprising a phenylenediamine photographic silver halide developing agent and a silver halide solvent comprising a cyclohexane containing an amino radical attached to the carbocyclic ring thereof and in addition to said amino radical, a polar substituent selected from the class consisting of an amino radical, a hydroxyl radical and a hydroxyalkyl radical.

10. A photographic developing composition as defined in claim 9 wherein said aqueous alkaline solution contains a color-forming compound capable of coupling with the oxidation products of said phenylenediamine silver halide developing agent to produce a colored image.

11. A photographic developing composition consisting of an aqueous alkaline solution comprising a p-N-phenylenediamine photographic silver halide developing agent and 1,4-bis(methylamino)cyclohexane.

12. A photographic developing composition as defined in claim 11 wherein said aqueous alkaline solution contains a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine developing agent to produce a colored image.

13. A photographic developing composition consisting of an aqueous alkaline solution comprising a p-phenylenediamine photographic silver halide developing agent and 4-aminocyclohexanol.

14. A photographic developing composition as defined in claim 13 wherein said aqueous alkaline solution contains a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine silver halide developing agent to produce a colored image.

15. A photographic developing composition consisting of an aqueous alkaline solution comprising a p-phenylenediamine photographic silver halide developing agent and 1-cyclohexylamino-2-propanol.

16. A photographic developing composition as defined in claim 15 wherein said aqueous alkaline solution contains a color-forming compound capable of coupling with the oxidation products of said p-phenylenediamine silver halide developing agent to produce a colored image.

17. In the reversal process of color photography for producing a colored image in a photoexposed multi-layer color material having sensitivity in discrete areas thereof in the red, green and blue regions, respectively, of the visible spectrum, by first developing a black-and-white negative image, followed by at least one development in a color developer to produce a color record, the step of incorporating in at least one of the developing compositions a silver halide solvent comprising a cyclohexane containing an amino radical attached to the carbocyclic ring thereof and in addition to said amino radical, a polar substituent selected from the class consisting of an amino radical, a hydroxyl radical and a hydroxyalkyl radical.

18. A process according to claim 17 wherein said silver halide solvent is 1,4-bis(methylamino)cyclohexane.

19. A process according to claim 17 wherein said silver halide solvent is 4-aminocyclohexanol.

20. A process according to claim 17 wherein said silver halide solvent is 1-cyclohexylamino-2-propanol.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,128,182

April 7, 1964

Charleton C. Bard 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 9, line 56, for "p-N-phenyl-" read -- p-phenyl- --.

Signed and sealed this 4th day of August 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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