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MAGNETA COLOR DEVELOPER SOLUTIONS

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U.S. Cl. 96—56.5 **9 Claims**

ABSTRACT OF THE DISCLOSURE

Hydroxylamine, or a mono-alkyl-substituted hydroxylamine, is utilized in photographic magenta-color-developing compositions which contain an N,N-dialkyl-substituted hydroxylamine as a balancing developing agent. The hydroxylamine or mono-alkyl-substituted hydroxylamine serves to improve the stability of the developing composition and substantially reduces the loss of coupler and color developing agent resulting from the presence of the balancing developing agent.

This invention is concerned with color photography and more particularly with compositions and processes used in magenta color development of color photographic materials during color processing.

In multilayer photographic elements used for color photography there are usually three selectively sensitized emulsion layers coated on one side of a photographic support. For example, the uppermost layer is generally blue sensitive, the next layer generally comprises a yellow filter and the next layer is generally green sensitive. The emulsion layer adjacent to the support is generally red sensitive. The yellow filter layer located between the blue and green sensitive layers serves to absorb the blue radiation which may be transmitted through the blue-sensitive layer to the underlying layers which are sensitive to the blue region of the spectrum in addition to the red or green regions of the spectrum. Some of these subject multilayer photographic elements contain additional silver halide emulsion layers for specialized purposes. In photographic print material, frequently the yellow filter layer is omitted and the arrangement of silver halide emulsion layers may be changed for the purpose of obtaining more accurate recording of the color negative. Multilayer materials of the type which can be used in the present invention have been previously described in the prior art, such as Mannes et al., U.S. Patent 2,252,718, issued Aug. 19, 1941.

Color material of the type employed in the present invention includes those which are intended primarily for reversal color process in which the exposed material is given a conventional black-and-white negative development, followed by a reversal re-exposure or exposures and finally color development. Usually, phenolic or naphtholic couplers are used to produce the cyan dye, open chain di-β-ketone couplers are generally used for producing yellow-dye images and 2-pyrazolin-5-one couplers generally are used to produce the magenta dye images. In the development step, the dye image is produced by contacting the reversal exposed silver halide with an aqueous alkaline developer solution containing a primary aromatic amine color developing agent in the presence of the appropriate color forming coupler.

In the processing of photographic color materials by a reversal technique in which the color-forming couplers are incorporated in the color developers, it is well known to use a balancing developing agent in one or more of the color developers. This practice is particularly common with respect to the cyan color developer; such balancing developers serve two functions in general, first, such balancing developing agents act as antioxidants and they frequently react with oxidized color developers through a cross-oxidation reaction which regenerates the desired color developing agents; secondly, such balancing developing agents react directly with the exposed silver halide as an auxiliary developing agent. The desired effect of using such balancing developing agents is to improve the photographic quality, for example, to decrease high light stain and/or to improve the sensitometric curve shape for the developed dye image. It is known to use N,N-diethylhydroxyl amine as a balancing developing agent in color developers. The use of this material produces valuable improvements in the photographic quality of the dye images produced; and although this compound produces no detrimental effect on the stability of the cyan and yellow color developer solutions, its presence in the magenta developer solution results in the destruction of substantial quantities of magenta couplers. This has made it necessary to increase the concentration of the coupler and the color developing agent in the replenisher solution used to maintain the desired concentration of these chemicals in the magenta color developer solution tank during continuous processing of color material.

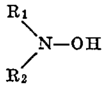
It is therefore an object of my invention to provide novel compositions for preparing magenta-color-forming developers which will produce more stable solutions. Still another object is to provide a novel magenta-color-forming composition comprising a 2-pyrazolin-5-one coupler, a N,N-dialkyl substituted hydroxylamine and a hydroxylamine or a mono-substituted hydroxylamine. Another object of my invention is to greatly improve the stability of the magenta coupler and color developing agent in magenta color developer solutions containing a N,N-dialkyl substituted hydroxylamine by adding a relatively small amount of a mono-substituted derivative of hydroxylamine, or hydroxylamine per se.

These and other objects of my invention are accomplished according to my invention by using a magenta color developer composition comprising (1) a 2-pyrazolin-5-one magenta-dye-forming coupler, (2) a water-soluble amine having the formula:

I $\qquad$ RNHOH

wherein R represents hydrogen or a lower alkyl group, preferably, having from 1 to 3 carbon atoms such as methyl, ethyl, propyl, etc., and water soluble acid salts of said amine, and (3) a compound having the formula:

II



wherein R_1 and R_2 represent the same or different lower alkyl groups having preferably from 1 to 3 carbon atoms, e.g., methyl, ethyl, propyl, etc., and water-soluble acid salts of said compounds.

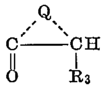
I have found that the desirable effects of the balancing developer of Formula II in my magenta color developer solutions can be maintained while the undesirable loss in magenta couplers and color developing agent is very substantially reduced, according to my invention, by the addition of relatively small amounts of the compounds of Formula I. Substantial savings in magenta couplers of as much as about 37% and about 16% savings in color developing agents have been made possible according to my invention.

Typical examples of compounds of Formula I include: hydroxylamine, ethylhydroxylamine, methylhydroxylamine, propylhydroxylamine, etc. Water soluble acid salts of compounds of Formula I are also used to advantage. It is understood, of course, that the acid used in making these salts preferably should not have any detrimental effect on photographic process or photographic material being processed. Included among the acid salts used to advantage are: sulfates, oxalates, chlorides, phosphates, carbonates, acetates, etc.

Typical compounds of Formula II include N,N-diethylhydroxylamine, N-ethyl-N-methylhydroxylamine, N-ethyl-N-propyl hydroxylamine, N,N-dimethylhydroxylamine, N,N-dipropylhydroxylamine, etc. Water soluble acid salts of compounds of Formula II are also used to advantage. These salts include any of the acid anions listed above.

Any of the well-known 2-pyrazolin-5-one magenta-forming couplers are used to advantage in my compositions. These magenta-forming couplers may contain any of the substituents commonly used on the 1, 3 and 4-positions providing, of course, that any substituent on the 4-position is displaced by reaction with oxidized color developing agent to form the image dye. These couplers include those represented by the formula

III



$$\begin{array}{ccc} & Q & \\ C & - & CH \\ \| & & | \\ O & & R_3 \end{array}$$

wherein Q represents the nonmetallic atoms required to complete any of the 2-pyrazolin-5-ones used in color photography and R_3 represents any member which will couple off when contacted with an aqueous solution containing oxidized primary aromatic amine color developing agent resulting in the formation of a magenta dye. R_3, includes hydrogen, chlorine, thiocyanate group, an aclyoxy group, a thioether group, an alkoxy group, etc.

Typical magenta-color-forming-2-pyrazolin-5-one couplers used to advantage according to my invention include the following:

1-p-sec. amylphenyl-3-n-2-pyrazolin-5-one
1-p-laurylphenyl-3-methyl-2-pyrazolin-5-one
1-β-naphthyl-3-amyl-2-pyrazolin-5-one
1-p-nitrophenyl-3-n-amyl-2-pyrazolin-5-one
1-p-phenoxyphenyl-3-n-amyl-2-pyrazolin-5-one
1-phenyl-3-n-amyl-2-pyrazolin-5-one
1,4-phenylene bis-3-(1-phenyl-2-pyrazolin-5-one)
1-phenyl-3-acetylamino-2-pyrazolin-5-one
1-phenyl-3-propionylamino-2-pyrazolin-5-one
1-phenyl-3-n-valerylamino-2-pyrazolin-5-one
1-phenyl-3-chloroacetylamino-2-pyrazolin-5-one
1-phenyl-3-dichloroacetylamino-2-pyrazolin-5-one
1-phenyl-3-benzoylamino-2-pyrazolin-5-one
1-phenyl-3-(m-aminobenzoyl)amino-2-pyrazolin-5-one
1-phenyl-3-(p-sec. amylbenzoylamino)-2-pyrazolin-5-one
1-phenyl-3-diamylbenzoylamino-2-pyrazolin-5-one
1-(2,4,6-trichlorophenyl)-3-(4-nitroanilino)-2-pyrazolin-5-one
1-phenyl-3-β-naphthoylamino-2-pyrazolin-5-one
1-phenyl-3-phenylcarbamylamino-2-pyrazolin-5-one
1-phenyl-3-palmitylamino-2-pyrazolin-5-one
1-phenyl-3-benzenesulfonylamino-2-pyrazolin-5-one
1-(p-phenoxyphenyl)-3-(p-tert. amyloxybenzoyl)amino-2-pyrazolin-5-one
3-(2,4-dichloroanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one
1-(2′,4′,6′-tribromophenyl)-3-benzamido-2-pyrazolin-5-one
1-(2′,4′,6′-trichlorophenyl)-3-benzamido-2-pyrazolin-5-one
1-(2′,4′,6′-trichlorophenyl)-3-phenylacetamido-2-pyrazolin-5-one
3-(4-cyanoanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one
1-(2′,4′,6′-tribromophenyl)-3-phenylacetamido-2-pyrazolin-5-one
1-(2′,4′-dichlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)benzamido]-2-pyrazolin-5-one
1-(2′,4′,6′-trichlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)benzamido]-2-pyrazolin-5-one
1-(2′,4′,6′-tribromophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)benzamido]-2-pyrazolin-5-one
1-(2′-4′-6′-trichlorophenyl)-3-[β-(2‴,4‴-di-tert. amylphenoxy)propionamido]-2-pyrazolin-5-one
1-(2′,4′,6′-tribromophenyl)-3-[β-(2‴,4‴-di-tert. amylphenoxy)propionamido]-2-pyrazolin-5-one
1-(2′,5′-dichloro)-3-[3″-(4‴-tert. amylphenoxy)benzamido]-2-pyrazolin-5-one
1-(2′,4′,6′-tribromophenyl)-3-[3″-(4‴-tert. amylphenoxy)benzamido]-2-pyrazolin-5-one
1-(2′,5′-dichlorophenyl)-3-[3″-(2‴,4‴-di-tert. amylphenoxyacetamido)benzamido]-2-pyrazolin-5-one.

The compounds of Formula I can be utilized in various concentrations depending upon the concentration of the balancing developer used, the concentration of the color developer, etc. In general, I have found that from about 0.10 to 2 g./liter of the compounds of Formula I are satisfactory for the purposes of my invention, the preferred concentration ranges being from about 0.4 to about 0.6 g./liter. The compounds of Formula II are used to advantage over concentration ranges of from about 0.5 to about 5 g./liter with a preferred range of from about 2.5 to about 3.1. The magenta coupler and color developer can be used over wide ranges of concentrations; however, usually the magenta coupler is used in the range from about 0.5 to about 2.9 g./liter and the color developing agent from about 0.8 to about 5 g./liter. The most advantageous concentration for the components of my magenta developing composition can be determined by developing a series of test strips of silver halide emulsion in developers having variations in the concentration of the coupler, the compounds of Formula I and the compounds of Formula II. This technique is well known in the art and need not be discussed further. The usual addenda can be employed in the developers, such as strong alkaline agents (e.g., sodium carbonate and sodium hydroxide), restraining agents (e.g., potassium bromide, potassium iodide, etc.), stain inhibitors, preservatives and antioxidants such as alkali metal sulfites, etc.

The compositions of my invention are used to advantage to prepare magenta-color-forming developer solutions used in the color processing of exposed multilayer, multicolor photographic elements. The elements contain gelatino-silver halide developing out emulsions, gelatino-silver chloride, -chlorobromide, -chloroiodide, -chlorobromoiodide, -bromide, and -bromoiodide developing out emulsions. These emulsions are coated in the usual manner on any suitable support, e.g., glass, cellulose nitrate film, cellulose ester film, polyvinyl ester resin film, paper, metal, etc. The silver halide emulsion layers may also contain such addenda as chemical sensitizers, e.g., sulfur sensitizers (e.g., allylthiocarbamide, thiourea, allylthiocyanate, cystine, etc.), various gold compounds (e.g., potassium chloroaurate, auric trichloride, etc.), (U.S. Patents 2,540,085; 2,597,856; 2,597,915), various azaindene compounds (such as, those discussed in U.S. Patent 2,716,062), condensation products of alkylene oxides, such as those shown in U.S. Patent 2,400,032 as well as the additives mentioned in Jones et al., U.S. Patent 2,937,089.

My magenta-forming color developer solutions are used to advantage in color processes involving the successive steps of a negative black-and-white development usually accomplished with a black-and-white hydroquinone and p-methylaminophenyl sulfate black-and-white developer, washing, selective re-exposure of the red-sensitive layer, cyan color development with an aqueous alkaline solution containing a primary aromatic amine color developing agent and a cyan coupler, washing, selective re-exposure of the blue-sensitive layer, yellow color development in an aqueous alkaline solution containing a primary aromatic amine color developing agent, a yellow-forming coupler, washing, exposure to white light, color development with my color developer, washing, bleaching in a conventional ferricyanide bleach, fixing in a conventional alkali metal thiosulfate fixing bath, washing and drying. The process may include a prehardener bath containing Formalin-bisulfite, followed by water wash preceding the black-and-white development step. Also the process may include a reversal auxiliary bath containing a chemical fogging agent, such as, an alkali metal borohydride, and an auxiliary developing agent in place of the exposure to white light.

My magneta color developing solutions may contain any of the well-known primary aromatic amino color developers, such as the p-phenylene diamines including the alkylphenylene diamines and alkyl toluene diamines. These developing agents are usually used in the salt form such as the hydrochloride or sulfates which are more stable than amines. The p-aminophenols and their substitution products may also be used where the amine group is unsubstituted. Included among the color developing agents are such typical examples as 2-amino-5-diethylamino toluene hydrochloride, N - ethyl-β-methanesulfonamidoethyl, 4 - aminoaniline sulfate, 4 - amino-N,N - diethyl - 3 - methylanilino hydrochloride, 4-amino - N - ethyl - N(β - methanesulfonamidoethyl), m-toluene sesquisulfatemonohydrate, 3 - methyl-p-aminodiethylanilino sulfate, 4 - amino - N - ethyl - N -(β-hydroxyethyl)anilino sulfate, N,N-dimethyl-p-phenylenediamine hydrochloride, etc.

The following typical examples still further illustrate my invention.

EXAMPLE 1

Light-image-exposed multilayer, multicolor photographic material comprising a support coated in succession with a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a bleachable yellow filter layer and a blue-sensitive silver halide emulsion layer that had been given conventional pre-hardening in a formaldehyde-bisulfite pre-hardener, washed, negative developed in a convention hydroquinone p-methylaminophenol sulfate developing solution, washed, exposed through the support to a red light to expose the undeveloped, unexposed silver halide in the red-sensitive layer, cyan developed in a conventional aqueous alkaline color developing solution containing a cyan-forming coupler and a primary aromatic amine color developing agent, water washed, given blue light exposure to the top blue-sensitive layer to expose the unexposed silver halide in that layer, developed in a conventional aqueous alkaline yellow color developer containing yellow color forming coupler and a primary aromatic amine color developing agent, washed, treated in a reversal auxiliary bath containing an auxiliary black-and-white developing agent and potassium borohydride, and washed, was given about 5 minutes magenta development in an aqueous alkaline developer solution comprising:

	G./liter
N,N-diethylhydroxylamine	2.8
Hydroxylamine	.5
3-(2,4-dichloroanilino) - 1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one	1.6
4 - amino - 3 - β - sulfonamidoethyl-N,N-diethylaniline	1.25

at about 90° F., the magenta developed material was then washed, given conventional ferricyanide bleaching, conventional alkali metal thiosulfate fixing, washed and dried. The processed color material had a good reproduction of the light image exposure. Optical density measurements made of the processed material showed that the magenta D-max was about 3.3 density units.

EXAMPLE 2

Example 1 was repeated using an aqueous alkaline magenta color developer containing from about 2.5 to about 3.1 g./liter of N,N-diethylhydroxylamine, from about .4 to about .6 g./liter of hydroxylamine, from about 1.5 to about 1.7 g./liter of the magenta coupler

used in Example 1 and from about 1 gram to about 1.5 g./liter of the color developing agent used in Example 1. The results were good being comparable to those obtained in Example 1.

EXAMPLE 3

Example 2 was repeated using the magenta coupler 1 - (2,4,6 - trichlorophenyl) - 3 - (4 - nitroanilino) - 2-pyrazolin-5-one in place of the magenta coupler used in Examples 1 and 2. Good image reproductions were obtained in the processed film which had good magenta D-maxes comparable to those of Examples 1 and 2. Used magenta developers from Examples 1 through 4 were noticeably cleaner than prior art developers. Magenta coupler recovered from the immediate used developer solutions was found to be purer than previously.

EXAMPLE 4

Example 3 was repeated excepting that the magenta coupler 3 - (4 - cyanoanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one was used in place of the magenta coupler used in Examples 1 and 2. The results showed good image reproductions in which magenta D-maxes were obtained that were comparable to those from the preceding examples.

Similarly, it can be shown that magenta color developers containing from about 0.1 to about 2 g./liter of other compounds of Formula I, from about 0.5 to about 5 g./liter of other compounds of Formula II and from about 0.5 to about 2.5 g./liter of any other magenta-color-forming couplers, and from about 0.8 to about 5 g./liter of other color developing agents will give good magenta color development.

The optimum concentrations for these chemicals in my magenta color developer can be determined readily as mentioned before and will depend upon the particular color photographic material being processed, the processing conditions used, the particular chemicals used in the magenta color developer and other factors.

My magenta developer can be used to advantage over a wide range of processing conditions such as, temperature, time, etc. The optimum conditions are determined by methods well known in the art.

During continuous processing of photographic materials it is common practice to maintain the optimum tank concentrations of the various components of the developers and other processing solutions by continually replenishing the processing solutions with replenisher solutions at carefully established and controlled rates. The replenisher solutions are so designed that their continuous addition to the respective tanks during the operation will compensate for the use of the various color developing agents, couplers, etc. by the color photographic material being processed and by aerial oxidation or other undesirable side reactions.

The unobvious advantages obtained by use of my magenta developer compositions are illustrated by the following table. The table shows the magenta replenisher concentrations which were required to maintain the optimum concentrations in a magenta color developer tank containing no compound of Formula I as compared to the concentrations required in a replenisher containing a compound of Formula I that were required to maintain the optimum concentrations in a magenta color developer tank containing a compound of Formula I (based on prolonged continuous operation).

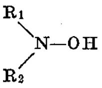
	Concentration in replenisher		Savings of chemical
	G./l.	G./l.	
Hydroxylamine	0	.86	
N,N-diethylhydroxylamine	4.5	4.1	About 10%.
3-(2,4-dichloroanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one.	4.6	2.9	About 37%.
4-amino 3-β-sulfonamidoethyl-N,N-diethylanilino.	3.1	2.6	About 16%.

In addition to these very important savings in the chemicals shown above from use of my magenta developer compositions, there are other important technical advances accomplished. For example, the immediate process gives more uniform magenta development resulting in improved photographic color quality. The magenta color developer solutions remain substantially cleaner during use than previously so the processed photographic material is cleaner and the processing machine tanks do not need to be cleaned as frequently. Furthermore, magenta coupler is recovered from my used magenta color developer solutions in a much purer form, and in higher yields than was possible from other used magenta developer solutions. It is not obvious that my magenta color developer compositions would provide these and other important technical advances.

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.

I claim:

1. An aqueous alkaline photographic developing solution comprising
   (1) a primary aromatic amino color developing agent,
   (2) a magenta-dye-forming 2-pyrazolin-5-one color coupler,
   (3) a member selected from the group consisting of compounds of the formula



$$R_1R_2N\text{—}OH$$

   and their water-soluble salts, wherein R_1 and R_2 each represent a lower alkyl group, and
   (4) a member selected from the group consisting of hydroxylamine and water-soluble salts thereof.

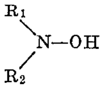
2. A developing solution as described in claim 1 wherein component (3) is N,N-diethylhydroxylamine.

3. A developing solution as described in claim 1 wherein component (3) is N,N-diethylhydroxylamine and component (4) is hydroxylamine sulfate.

4. A developing solution as described in claim 1 wherein component (2) is 3-(2,4-dichloroanilino)-1-(2,4,6-trichlorophenyl)-2-pyrazolin-5-one, component (3) is N,N-diethylhydroxylamine, and component (4) is hydroxylamine sulfate.

5. A developing solution as described in claim 1 wherein component (1) is present in an amount of from about 0.8 to about 5 grams per liter, component (2) is present in an amount of from about 0.5 to about 2.9 grams per liter, component (3) is present in an amount of from about 0.5 to about 5 grams per liter, and component (4) is present in an amount of from about 0.1 to about 2 grams per liter.

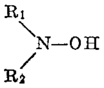
6. In an aqueous alkaline photographic developing solution comprising a primary aromatic amino color developing agent, a magenta-dye-forming 2-pyrazolin-5-one color coupler, and a member selected from the group consisting of compounds of the formula



$$R_1R_2N\text{—}OH$$

and their water-soluble salts, wherein R_1 and R_2 each represent a lower alkyl group, the improvement comprising the addition of a member selected from the group consisting of hydroxylamine and water-soluble salts thereof.

7. A process for magenta color developing a light image exposed hydrophilic colloid silver halide emulsion layer comprising contacting said layer with an aqueous alkaline developing solution comprising
   (1) a primary aromatic amino color developing agent,
   (2) a magenta-dye-forming 2-pyrazolin-5-one color coupler,
   (3) a member selected from the group consisting of compounds of the formula



$$R_1R_2N\text{—}OH$$

   and their water-soluble salts, wherein R_1 and R_2 each represent a lower alkyl group, and
   (4) a member selected from the group consisting of hydroxylamine and water-soluble salts thereof.

8. A process as described in claim 7 wherein component (3) is N,N-diethylhydroxylamine.

9. A process as described in claim 7 wherein component (3) is N,N-diethylhydroxylamine and component (4) is hydroxylamine sulfate.

References Cited

UNITED STATES PATENTS

3,141,771	7/1964	Bard et al.	96—22
3,300,305	1/1967	Pesch et al.	96—55

FOREIGN PATENTS

830,625	3/1960	Great Britain.

J. TRAVIS BROWN, Primary Examiner

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