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PHOTOGRAPHIC DEVELOPER CONTAINING A PYRIDINIUM SALT AND PROCESS OF DEVELOPMENT

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18 Claims. (Cl. 95—88)

1

This invention relates to photographic developers, and more particularly to accelerators for photographic developers.

In the development of photographic materials, it is often desired to accelerate the rate of development and to increase the effective photographic speed of the developed materials. However, the accelerators known so far to the art increase not only the effective emulsion speed, but also the contrast of the developed emulsion. The latter characteristic, namely, the increased contrast is seldom desirable since it affects the visual appearance of the picture to the extent that the pleasing middle tones and details in the shadow and high light areas are frequently lost. Moreover, many of the known accelerators increase the pH of the developer solution, a feature which is always undesirable. In fact, the accelerating action of many of the known accelerators is very largely due to the increased pH and the results, as undesirable as they may be at times, can be duplicated more simply and economically by adding more alkali, such as sodium carbonate to the developing solution.

It is also known that various quaternary ammonium salts may be added to photographic black and white and color developing solutions. For example, quaternary ammonium salts of benzothiazole or aminobenzothiazole tend to decrease graininess; pyridinium salts substituted by a phenylene diamine or an aminophenol radical act as developing agents; surface active quaternary ammonium salts having a long chain hydrocarbon radical attached to the pentavalent nitrogen atom change the color of dye images obtained by color coupling development, and surface active pyridinium salts substituted by a hydrophilic group of more than eight carbon atoms restrain development in the shoulder density region. In other words, the quaternary ammonium salts disclosed and suggested, impart to the photographic developing solutions, new properties which cause a change in the photographic characteristics of the developed photographic materials. However, these otherwise desirable changes are commonly accompanied by a loss of speed, drastic changes in gradation and loss of maximum density.

It is, therefore, an object of the present invention to provide black and white and color developers having an increased rate of development so that a greater effective speed is imparted to the developed photographic material without increase in contrast.

It is another object of the invention to provide black and white and color developers having an increased rate of development so that the development time is substantially decreased.

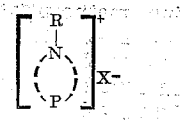
2

Other objects will become apparent from the following description:

The above objects are accomplished by adding to the usual black and white developer and to alkaline color forming developers in which a primary aromatic amine is used as the developing agent, a quaternary pyridinium salt having a short chain aliphatic radical of not more than five carbon atoms attached to the pentavalent nitrogen atom. It has been found that developer solutions containing quaternary pyridinium salts increase the rate of development in black and white developers, for instance, Metol and hydroquinone and the like, and provide greater effective speed in the developed materials without any concurrent increase in contrast. It has also been found that in developing color images in multi-color photographic layers containing color formers fast to diffusion, as disclosed in United States Patents 2,178,612; 2,179,228; 2,179,234; 2,179,238–9; 2,179,244; 2,186,719; 2,186,851–2; 2,186,732–4; 2,186,849; 2,200,306; 2,280,722; 2,292,575; 2,303,928 and 2,307,399 with an alkaline color developer solution containing a primary aromatic amine as the developing agent and a pyridinium salt having a short chain alkyl substituent on the pentavalent nitrogen atom, the effective increase in speed is obtained without any change in contrast. All of the layers are developed simultaneously and the images formed are of excellent quality. Correspondingly, when no increase in speed is desired, the developing time with black and white and color developers can be reduced to less than half by the addition of a pyridinium salt to the developer.

Another valuable characteristic property of the pyridinium salts is their ability to prolong the useful life of developing solutions, especially when used as constituents of both the developer and the replenisher solution.

The pyridinium salts to be employed in accordance with the present invention are represented by the following general formula:



wherein P represents the atoms necessary to complete an unsubstituted pyridinium nucleus, an alkoxy-substituted pyridinium nucleus, e. g., a 2-methoxy-, 3-methoxy-, 4-methoxy, 2-ethoxy-,

3-ethoxy-, 2,4-dimethoxy-, 2,4-diethoxy-, 2,5-diethoxy-, or 3,5-diethoxy-pyridinium nucleus; a picolinium nucleus, e. g., a 4-methyl-, 2-methyl-, or 3-methyl-pyridinium nucleus; a lutidinium nucleus, e. g., a 2,3-dimethyl-, 2,4-dimethyl-, 2,5-dimethyl-, 2,6-dimethyl-, 3,4-dimethyl-, 3,5-dimethyl-, 2-ethyl-, 3-ethyl- or 4-ethyl-pyridinium nucleus; a collidinium nucleus, e. g., a 2-propyl-, 2-isopropyl-, 4-methyl-2-ethyl-, 4-methyl-3-ethyl-, 2-methyl-4-ethyl-, 2-methyl-5-ethyl-, 2-methyl-6-ethyl-, 2,3,4-trimethyl-, or 2,3,6-trimethyl-pyridinium nucleus, or a parvolinium nucleus, e. g., a 2-butyl-, 2-isobutyl-, 3,5-dimethyl-2-ethyl, 2,6-dimethyl-3-ethyl-, 2,6-dimethyl-4-ethyl-, 2,4-diethyl- or 3,4-diethyl-pyridinium nucleus; wherein R is a short chain aliphatic radical having not more than 5 carbon atoms, such as alkyl, e. g., methyl, ethyl, propyl, butyl or amyl; chloro- or bromoalkyl, e. g., β-chloroethyl, β-bromoethyl, γ-chloropropyl or γ-bromopropyl; hydroxyalkyl, e. g., β-hydroxyethyl, β-hydroxypropyl, or β,γ-dihydroxypropyl, carboxymethyl; carbalkoxymethyl, e. g., carbomethoxymethyl, carbethoxymethyl or carbopropoxymethyl, carboxamidomethyl; N-substituted carboxamidomethyl, e. g., N,N-dimethylcarboxamidomethyl; alkoxyalkyl, e. g., methoxymethyl, ethoxymethyl, ethoxyethel or propoxymethyl; and wherein X represents an anion selected from the group consisting of chloride, bromide thiocyanate, methosulfate and thiocyanate.

The following is merely a suggestive listing of pyridinium salts which may be employed for the purpose herein set forth:

1-methylpyridinium chloride.
1-ethylpyridinium bromide.
1-(β-chlorethyl) pyridinium chloride.
1-(1-β-bromethyl) pyridinium bromide.
1-propylpyridinium bromide.
1-(β-hydroxyethyl) pyridinium chloride.
1-methoxymethylpyridinium bromide.
1-ethoxymethylpyridinium bromide.
1-propoxymethylpyridinium bromide.
1-(β-acetoxyethyl) pyridinium chloride.
1-(β,γ-dihydroxypropyl) pyridinium chloride.
1-carboxymethylpyridinium chloride.
1-carboxymethylpyridinium bromide.
1-carbomethoxymethylpyridinium bromide.
1-carbethoxymethylpyridinium chloride.
1-methyl-2-methylpyridinium chloride.
1-methyl-2-methylpyridinium bromide.
1-methyl-3-methylpyridinium bromide.
1-methyl-4-methylpyridinium bromide.
1-ethyl-2-methylpyridinium bromide.
1-ethyl-4-methylpyridinium bromide.
1-carboxymethyl-2-methoxypyridinium bromide.
1-carboxymethyl-3-methylpyridinium chloride.
1-carboxymethyl-2-methylpyridinium chloride.
1-carboxymethyl-2-methylpyridinium thiocyanate.
1-carbethoxymethyl-3-picolinium chloride.
1-methyl-3-ethylpyridinium chloride.
1-carboxymethyl-3-ethylpyridinium chloride.
1-(β-hydroxyethyl)-2-methylpyridinium bromide.
1,2,3-trimethylpyridinium methosulfate.
1,2,4-trimethylpyridinium methosulfate.
1,2,5-trimethylpyridinium methosulfate.
1,2,6-trimethylpyridinium methosulfate.
1,3,5-trimethylpyridinium methosulfate.
1-ethyl-2,3-dimethylpyridinium ethosulfate.
1-ethyl-2,4-dimethylpyridinium ethosulfate.
1-ethyl-2,5-dimethylpyridinium ethosulfate.
1-ethyl-2,6-dimethylpyridinium ethosulfate.

1-ethyl-3,5-dimethylpyridinium ethosulfate.
1-methyl-2-propylpyridinium chloride.
1-methyl-2-isopropylpyridinium bromide.
1-hydroxyethyl-2-methyl-5-ethylpyridinium chloride.
1,5-diethyl-2-methylpyridinium bromide.
1,4-dimethyl-3-ethylpyridinium bromide.
1,2,4,6-tetramethylpyridinium bromide.
1-methyl-2-methoxypyridinium methosulfate.
1-ethyl-3-methoxypyridinium ethosulfate.
1-ethyl-3-methoxypyridinium bromide.
1-carboxymethyl-2-ethoxypyridinium chloride.
1-carbethoxymethyl-2-ethoxypyridinium chloride.
1-methyl-2,4-dimethoxypyridinium methosulfate..
1-acetamido-2,4-diethoxypyridinium chloride.
1-ethyl-2,5-diethoxypyridinium ethosulfate.
1-carbethoxymethyl-3,5-diethoxypyridinium chloride.

The foregoing quaternary pyridinium salts in which the nitrogen atom occupies the 1-position are prepared by reacting pyridine or a substituted pyridine, e. g., a picoline, a lutidine, a collidine, a parvoline or an alkoxypyridine with a quaternizing agent, e. g., an alkyl chloride, alkyl bromide, dimethyl sulfate, diethyl sulfate, chloroacetic acid, methyl chloroacetate, ethyl chloroacetate, chloroacetamide and the like. The quaternization may be carried out by heating or at room temperature in the presence of suitable solvent diluents, such as ether, benzene, toluene, xylene and the like, or under pressure at elevated temperatures depending on the relative reactivity of the ingredients. The chlorides and bromides may also be obtained by first preparing the corresponding iodide and subsequently converting it by the use of the appropriate silver halide. The thiocyanates are prepared by the addition of alkali thiocyanate to the solution of a more soluble quaternary salt.

The quaternary pyridinium salts are readily soluble in water and in alkaline solutions and can be used in concentrations varying from 0.3 gram per liter to the limit of their solubility in alkaline developer solutions. However, it has been found that for practical results, concentrations ranging from 0.5 gram to 7 grams per liter of developer solution are the most useful.

The following examples will illustrate developing solutions containing such quaternary pyridinium salts.

Example I

	Grams
p-Monomethylaminophenol sulfate	1.5
Hydroquinone	3.0
Sodium sulfite (anhydrous)	45.0
Sodium carbonate (monohydrate)	6.0
Potassium bromide	0.8
1-ethyl-2-methylpyridinium chloride	0.5
Water to make 1 liter	

This tank developer gives, on 6 to 8 minutes development of a roll film at 20° C. followed by washing and fixing, a negative having an ASA speed rating of about 96. Increasing the concentration of the 1-ethyl-2-methylpyridinium salt to 5.0 grams per liter of developer solution produced a negative having an ASA speed rating of 128. The omission of the 1-ethyl-2-methylpyridinium chloride from the developer solution leads, under otherwise identical conditions, to a negative having an ASA speed rating of only 64.

Example II

The useful life of the developers containing the 1-ethyl-2-methylpyridinium salt could be lengthened to the extent that it permitted the development of 25 rolls of exposed film without showing any speed loss or change of gradation by the gradual addition of a replenisher having the following composition:

	Grams
p-Monomethylaminophenol sulfate	3.0
Hydroquinone	6.0
Sodium sulfite	45.0
Sodium carbonate (monohydrate)	12.0
1-ethyl-2-methylpyridinium chloride	5.0
Water to make 1 liter	

When the pyridinium salt was omitted from both the developer and the replenisher, a speed loss corresponding to at least one half stop and an increase in the contrast of the developed film were noted after the development of about 10 rolls of film. In other words, the use of 1-ethyl-2-methylpyridinium chloride (in both the developer and the replenisher solutions) increased the useful life of the developer solution by a factor of 2.5.

Example III

	Grams
p-Monomethylaminophenol sulfate	0.8
Hydroquinone	1.2
Sodium sulfite (anhydrous)	45.0
Potassium metabisulfite	4.0
Sodium carbonate (monohydrate)	8.0
Water to make 1 liter	

The addition of 5 grams of 1-(β-hydroxyethyl) pyridinium chloride to this solution accelerated the developing rate and increased the effective photographic speed of a developed roll film by 100% when compared with the speed of a similar roll film processed in a developer containing no pyridinium salt.

Example IV

	Grams
N-ethyl-N-β-hydroxyethyl-p-phenylenediamine sulfate	6.7
Sodium hexametaphosphate	1.0
Sodium bisulfite	2.0
Sodium carbonate	100.0
Hydroxylamine hydrochloride	1.0
Potassium bromide	1.0
Water to make 1 liter	

This color developer was used for the development of an exposed color negative film at a temperature of 20° C. After developing for 20 minutes, a negative having an ASA speed rating of 10 was obtained. By adding 2 grams of 1,2-dimethylpyridinium methosulfate to the same developer solution, an image was developed in a similar color film which has an ASA speed rating of 18 without noticeably changing the gradation or the balance of the developed picture. The color photographic multilayer element used in the foregoing example consists of an integral tripack emulsion coated on a clear cellulose acetate or nitrate film base. Each of the emulsion layers is sensitized to one of the primary colors of light, namely, blue, green and red. The top layer is blue sensitive, the middle layer is green sensitive, and the bottom layer is red sensitive. The green sensitive and blue sensitive emulsion layers are separated by a yellow, blue absorbing filter layer. Each of the three silver halide emulsion layers contains dye forming compounds which unite during the development of the silver image in a primary aromatic amino developing agent to form a dye with the oxidation product of the developing agent. A yellow dye is formed in the blue sensitive emulsion layer, a magenta dye is formed in the green sensitive emulsion, and a cyan dye is formed in the red sensitive emulsion. The combination of the dye images from these printing primaries yields the color picture after the removal of the developed silver by bleaching, followed by fixing. Suitable methods for the preparation of multi-color emulsion layers have been described in the literature relating to color photography and are, therefore, not described here.

Example V

	Grams
p-Amino-di(β-hydroxyethyl) aniline sulfate	6.0
Sodium hexametasulfate	1.0
Sodium bisulfite	2.0
Sodium carbonate (monohydrate)	100.0
Hydroxylamine hydrochloride	1.0
Potassium bromide	1.0
Water to make 1 liter	

A color paper, similar in construction to the color film described in Example IV with the exception that the three emulsions were coated on a paper base, was developed for 20 minutes at 20° C. in the above developer. By the addition of 3.0 grams of 1-carboxymethyl-2-methylpyridinium bromide to a similar developer, the increase in the effective photographic speed of the developed material was by a factor of 2, without a noticeable change of contrast or loss of color balance.

Example VI

A color positive film coated on a white opaque base but otherwise similar in construction to the negative film used in Example IV, was exposed through a color transparency and developed for 18 minutes at a temperature of 20° C. in a developer having the following composition:

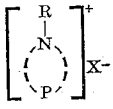
	Grams
4-diethylaminoaniline hydrochloride	6.0
Sodium hexametasulfate	1.0
Sodium bisulfite	2.0
Sodium carbonate	100.0
Hydroxylamine hydrochloride	1.0
Water to make 1 liter	

By adding 2.0 grams of 1-(carbethoxymethyl)-2-methylpyridinium thiocyanate, the increase in the effective photographic speed of the developed color material was by 50% without any increase of contrast or loss of color balance. By increasing the amount of added pyridinium salt to 6.0 grams, it is possible to increase the effective photographic speed of the developed opaque material by 100% without noticeable change in contrast. Concentrations of over 7.0 grams per liter tend to destroy the color balance.

The above examples are to be regarded as merely illustrative of the invention and not in any sense restricted. It will be obvious to those skilled in the art that many modifications, such as substituting equivalent materials and varying the proportions of the materials used, are within the spirit and scope of the invention which is to be limited solely by the following claims.

We claim:

1. An alkaline photographic developer for silver halide emulsions comprising an aromatic silver halide developing agent and a pyridinium salt selected from the class consisting of those corresponding to the following general formula:



wherein P represents the atoms necessary to complete a heterocyclic ring structure selected from the class consisting of pyridinium, picolinium, lutidinium, collidinium, parvolinium and alkoxy-substituted pyridinium radicals, R represents an aliphatic radical of not more than 5 carbon atoms, said radical selected from the group consisting of alkyl, chloroalkyl, bromoalkyl, hydroxyalkyl, carboxymethyl, carbalkoxymethyl and alkoxyalkyl, and X is an anion selected from the class consisting of chloride, bromide, thiocyanate, methosulfate and ethosulfate.

2. An alkaline photographic developer for a silver halide emulsion comprising an aromatic silver halide developing agent and 1-ethyl-2-methylpyridinium chloride.

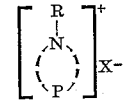
3. An alkaline photographic developer for a silver halide emulsion comprising an aromatic silver halide developing agent and 1-(β-hydroxyethyl) pyridinium chloride.

4. An alkaline photographic developer for a silver halide emulsion comprising an aromatic silver halide developing agent and 1,2-dimethylpyridinium methosulfate.

5. An alkaline photographic developer for a silver halide emulsion comprising an aromatic silver halide developing agent and 1-carboxymethyl-2-methylpyridinium bromide.

6. An alkaline photographic developer for a silver halide emulsion comprising an aromatic silver halide developing agent and 1-(carbethoxymethyl)-2-methylpyridinium thiocyanate.

7. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and a developing accelerator selected from the class consisting of those having the following formula:



wherein P represents the atoms necessary to complete a heterocyclic ring structure selected from the class consisting of pyridinium, picolinium, lutidinium, collidinium, parvolinium and alkoxy-substituted pyridinium radicals, R represents an aliphatic radical of not more than 5 carbon atoms, said radical selected from the group consisting of alkyl, chloroalkyl, bromoalkyl, hydroxyalkyl, carboxymethyl, carbalkoxymethyl and alkoxyalkyl, and X is an anion selected from the class consisting of chloride, bromide, thiocyanate, methosulfate and ethosulfate.

8. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and 1-ethyl-2-methylpyridinium chloride.

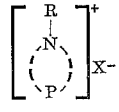
9. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and 1-(β-hydroxyethyl) pyridinium chloride.

10. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and 1,2-dimethylpyridinium methosulfate.

11. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and 1-carboxymethyl-2-methylpyridinium bromide.

12. In the development of a photographic image, the step comprising the development of an exposed silver halide emulsion in an alkaline developer containing an aromatic silver halide developing agent for said emulsion and 1-(carbethoxymethyl) - 2 - methylpyridinium thiocyanate.

13. A color forming photographic developer comprising a primary amino silver halide developing agent and a pyridinium salt selected from the class consisting of those having the following formula:



wherein P represents the atoms necessary to complete a heterocyclic ring structure selected from the class consisting of pyridinium, picolinium, lutidinium, collidinium, parvolinium and alkoxy-substituted pyridinium radicals, R represents an aliphatic radical of not more than 5 carbon atoms, said radical selected from the group consisting of alkyl, chloroalkyl, bromoalkyl, hydroxyalkyl, carboxymethyl, carbalkoxymethyl and alkoxyalkyl, and X is an anion selected from the class consisting of chloride, bromide, thiocyanate, methosulfate and ethosulfate.

14. A color forming photographic developer comprising a primary aromatic amino silver halide developing agent and 1-ethyl-2-methylpyridinium chloride.

15. A color forming photographic developer comprising a primary aromatic amino silver halide developing agent and 1-(β-hydroxyethyl)-pyridinium chloride.

16. A color forming photographic developer comprising a primary aromatic amino silver halide developing agent and 1,2-dimethylpyridinium methosulfate.

17. A color forming photographic developer comprising a primary aromatic amino silver halide developing agent and 1-carboxymethyl-2-methylpyridinium bromide.

18. A color forming photographic developer comprising a primary aromatic amino silver halide developing agent and 1-(carbethoxymethyl)-2-methylpyridinium thiocyanate.

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