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PHOTOGRAPHIC DEVELOPER

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ABSTRACT OF THE DISCLOSURE

The present invention is directed toward a photographic developing agent consisting of the following compound:

$$R_1—N=(R_2)(R_3)$$

where R_1 and R_2 are phenyl groups consisting of those which are substituted in ortho and para positions by hydroxy, amino, alkyl and alkoxy groups having from 1 to 5 carbon atoms, and R_3 represents hydrogen, methyl, ethyl, propyl, ethoxy or propoxy.

The present invention relates to a photographic developer and it particularly relates to the development of latent images produced by exposure to radiation in silver halide photographic emulsions.

It is among the objects of the present invention to provide photographic developing agents which require less exposure, and which will most faithfully reproduce the image of the object.

Still further objects and advantages will appear in the more detailed decription set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In accomplishing the above objects, it has been found most satisfactory to treat the photographic emulsion with a developing compound having the following formulae:

FORMULA I

$$R_1—N=C(R_2)R_3$$

of

FORMULA II

$$HO.C_6H_4—N=CH.C_6H_4.R_4$$

In the above formulae, R_1 and R_3 are phenyl radicals having single or multiple substitutions of hydroxy or amino groups in either ortho or para positions. R_2 may be hydrogen, alkyl having 1 to 5 carbon atoms, phenyl with either substituted hydroxy or amino groups, or both in ortho or para positions to each other, or a fatty acid radical having 1 to 3 carbon atoms. R_4 may be one or more hydroxy or alkoxy groups having 1 to 5 carbon atoms.

The preferred compounds are those that are produced by reactions between para-aminophenol on one hand and various substituted benzaldehydes on the other. The benzaldehyde must be substituted by hydroxy and amino groups in para or ortho position, and may or may not be substituted in other positions by alkoxy groups, sulfonic groups or carboxylic groups.

The resultant compounds, upon oxidation, whether by the latent image in the photographic emulsion or by other means, will produce conjugation of unsaturation running between the two substituted cyclic phenyl groups. As a result, a quinoidal group will be formed.

As typical of the compounds which have been found particularly satisfactory are the following:

FORMULA III

$$HO—C_6H_4—N=CH.C_6H_4.OH$$

para-hydroxy benzalpara hydroxy aniline

FORMULA IV

$$HO—C_6H_4—N=CH—C\ H_4OH$$

ortho-hydroxy benzal para hydroxy aniline

FORMULA V

$$HO—C_6H_4—N=CH.C_6H_3(OCH_3).OH$$

3-methoxy-4 hydroxy benzal para-hydroxy-aniline

These compounds specifically may be produced as follows:

Example VI

Two aqueous solutions are made up as follows:

Solution VII.—21.8 grams of p-aminophenol, 1 gram sodium sulfite, and 20 cc. HCl (37%) are dissolved in 200 cc. water.

Solution VIII.—24.4 grams of p-hydroxybenzaldehyde, and 8 grams of sodium hydroxide are dissolved in 200 cc. water.

Both solutions are warmed to 40 to 45° C. and solution VII is added with stirring to solution VIII. A thick yellow orange precipitate is thrown down and the stirring is continued for ten minutes.

By the addition dropwise of a 10% solution of sodium hydroxide to adjust to a pH of 6.5 to 7, essentially all of the product is thrown out of solution.

The precipitate is filtered off with suction and washed thoroughly with 200 cc. of cold water to which has been added 1 gram of sodium sulfite. The filtered precipitate is now spread out and allowed to dry in a current of warm air.

Yield—40.4 grams (94.8% of theoretical) of Formula III.

Example IX

Two aqueous solutions are made up as follows:

Solution X.—10.9 grams of p-aminophenol, .5 gram of sodium sulfite, and 10 cc. HCl (37%) are dissolved in 100 cc. of water.

Solution XI.—1.2 grams of o-hydroxy benzaldehyde, and 4 grams of sodium hydroxide are dissolved in 150 cc. of water.

Both of the above solutions are brought to a temperature of 20° C. and solution X is added with stirring to solution XI. The pH is adjusted by additions of 10% sodium carbonate to a pH of 6.5–7.0 and the stirring continued another ten minutes. The light yellow precipitate is filtered off and washed with two portions of 100 cc. cold water having .5 gram sodium sulphite dissolved in it.

The precipitate is then spread out and allowed to dry.

Yield—19.4 grams (91% of theoretical) of Formula IV.

Example XII.

Two aqueous solutions are made up as follows:

Solution XIII.—21.8 grams of p-amino phenol, 1 gram sodium sulphite, and 20 cc. HCl (37%) are dissolved in 200 cc. of water.

Solution XIV.—30.4 grams of 4-hydroxy 3-methoxy benzaldehyde, and 8 grams of sodium hydroxide are dissolved in 250 cc. of water.

Solution XIII is added with stirring to solution XIV. After all of the first solution has been added, the pH of the mixture is adjusted to 6.5–7.0 with additions of 10% sodium carbonate solution. Stirring is continued an additional ten minutes and the precipitate is then filtered off. The precipitate is washed with two 100 cc. portions of

cold water in which is dissolved .5 gram of sodium sulphite. The precipitate is then spread out to dry. It is a tannish yellow color.

Yield—44.5 grams (93.6% of theoretical) of Formula V.

The above compounds may be used by themselves as the sole developing agents in suitable compositions as well as in conjunction with other developing agents as in the following example:

Example XIII

Developing agent	Parts by weight	
	Range	Preferred
Formula I	2-20	10
Sodium sulphite	30-60	40
Sodium carbonate	0-95	60
Sodium hydroxide	0.06-10	3.7
Potassium bromide	0.2-1.0	0.5
Water to make	1,000	1,000

The above solution may be diluted for use with from one to two parts of water and will develop at 65° F. in from one to four minutes, depending upon emulsion used and gamma desired.

The contrast and densities obtainable in the above composition may be altered by increase of the Formula I, decrease or increase of the sodium carbonate, and or the increase of dilution, time of development, and regulation of temperature.

In using the above compounds, the following preparations may be employed:

Example XIV

Developing agent	Parts by weight	
	Range	Preferred
Formula III	½-2	1
Hydroquinone	4-12	8.8
Sodium sulphite	35-60	45
Sodium carbonate	20-60	40
Potassium bromide	0.2-10	0.5
Sodium hydroxide	0.2-0.6	37
Water	1,000	1,000

The above example shows the use of the developing agent of the present invention with other known developing agents.

The development with the above solution may vary from 2½ to 5 minutes, depending upon the specific photographic emulsion and the contrast desired.

Example XV

Developing agent	Parts by weight	
	Range	Preferred
Formula I	2-8	4
Sodium sulphite	0.2-4	2
Sodium hydroxide	1-3	1.5
Sodium carbonate	10-30	20
Potassium bromide	1-3	2
Water	1,000	1,000

The oxidation products of the above developers resulting from the reduction of the latent image, are capable of insolubilizing or tanning colloids, such as gelatin. Therefore, these developers are useful in preferentially tanning gelatin in accordance with the image impressed thereon.

The above composition may be used at 65° F. for a development time of four minutes on an unhardened emulsion film which is exposed through the base. After development, the film is washed in cold running water, at room temperature, for five minutes, and then placed in a tray of hot water at 110° to 120° F., or hotter if necessary. The unhardened emulsion will start to dissolve and, with the application of two other baths of hot water at the same temperature, all of the unhardened emulsion will be dissolved away, leaving a hardened portion of emulsion adhering to the film base.

Then the film is put into cold water and into an acid hardening fixing bath. If desired, the silver may be removed with standard methods using permanganate-chloride-sulphuric acid, chromic acid, ferricyanide bleaches, or other oxidizing bleaches.

The compounds above stated in all of the foregoing examples will give unusually sharp images with even very short exposure periods and very weak latent images. The developed image will be greatly enhanced and will be sharply defined using the preferred compounds set forth in Formulae III, IV and V. Other groups may be substituted so as to enhance the properties of the developing compound, for example, the solubility, changes of immobility and increased reduction energy.

The preferred compound should be capable of forming quinoid structures in both phenyl radicals at both ends of the molecule.

The general formula may be considered as follows:

FORMULA XVI

$$HO—C_6H_4—N=CH—C_6H_4—OH$$

I will be noted that at each end of the molecule there is a substituted phenyl group, namely C_6H_4, which will have a hydroxy group preferably in para but also possibly in ortho position in respect to the connecting bond, which is —N=CH.

The Formula XVI with oxidization may readily convert to the formulation which will function most actively as the quinoidal compound, as follows:

FORMULA XVII

$$O=C_6H_4=N—CH=C_6H_4=O$$

These developers act as super compensating developing agents to produce useful contrast gradations in both over and under exposure conditions.

The developing compounds of the present invention are greatly superior to Metol (1-methylamino-4-hydroxybenzene) in that the compounds exhibit a higher reduction potential, an increase in resultant densities, and avoid allergic effects commonly associated with Metol.

Although sulphite in the above formulations may be omitted, it is desirably included to prevent an oxidation of the developing agent.

As many changes could be made in the above formulations and many apparently widely different embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. In the process of photographic reproduction which comprises exposing and developing a silver halide emulsion, the improvement wherein the developing agent is a compound of the following formula:

$$R_1—N=C(R_2)(R_3)$$

where R_1 and R_2 are selected from phenyl groups consisting of those which are substituted in ortho and para positions by hydroxy, amino, alkyl, and alkoxy groups having from 1 to 5 carbons atoms, and R_3 represents hydrogen, mehtyl, ethyl, propyl, ethoxy or propoxy.

2. A developing solution containing the compound of the following formula:

$$R_1—N=C(R_2)(R_3)$$

where R_1 and R_2 are selected from phenyl groups consisting of those which are substituted in ortho and para positions by hydroxy, amino, alkyl and alkoxy groups having from 1 to 5 carbon atoms and R_3 represents hydrogen, methyl, ethyl, propyl, ethoxy or propoxy, together with hydroquinone, sodium sulfite, sodium carbonate, and potassium bromide, all dissolved in water.

3. A developing solution containing the compound of the following formula:

$$R_1—N=C(R_2)(R_3)$$

where R_1 and R_2 are selected from phenyl groups consisting of those which are substituted in ortho and para positions by hydroxy, amino, alkyl and alkoxy groups having from 1 to 5 carbon atoms, and R_3 represents hydrogen, methyl, ethyl, propyl, ethoxy or propoxy, together with an additional developing agent, sodium sulfite, sodium carbonate and potassium bromide, all dissolved in water.

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