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2,695,234

PHOTOGRAPHIC DEVELOPMENT

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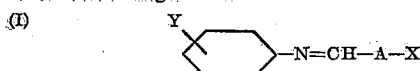
10 Claims. (Cl. 95—88)

This invention relates to a photographic developing process and to photographic developers, especially for use in color photography.

The p-phenylene diamines which are used as color developing agents have a number of drawbacks. They are highly allergic to the skin. Developing solutions which contain p-phenylene diamines darken which is due to oxidation by air, and at the same time the potency of the solution is diminished.

In order to avoid these disadvantages, it has been proposed to introduce into the molecule of the developing agent, either into the nucleus or into the substituents of the amino group, acidic groups which render the developing agents more water-soluble. However, in most of these cases, the developing power is substantially reduced by such introduction.

A further proposal is to introduce substituents containing acidic groups into the free NH₂ groups of the developing agents. Such developing agents correspond to the following formula:



wherein A is a divalent hydrocarbon nucleus; X is —COOM or —SO₃M (wherein M is hydrogen or a water-soluble salt-forming cation, preferably an alkali metal such as sodium or potassium); and Y is —OH, —NH₂, —NHR or —NR₂ in ortho- or para-position to the nitrogen atom (wherein R is a hydrocarbon radical).

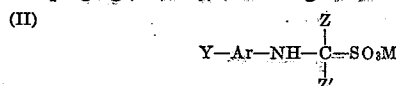
It is an object of our present invention to provide a new process for developing a reducible silver salt image in a photographic silver halide emulsion layer.

It is another object of our invention to provide a new process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer.

It is a further object of the invention to provide new photographic developing solutions.

Further objects will become apparent from the following description.

According to our invention, a reducible silver salt image is developed in a solution which contains a developing agent of the following formula:



wherein M is hydrogen or a water-soluble salt-forming cation, preferably an alkali metal such as sodium and potassium; Ar is a benzenoid radical, optionally substituted; Y is —NH₂, —NHR or —NR₂ and stands in para-position to the nitrogen atom (wherein R and R' is a hydrocarbon radical, optionally substituted or linked to the carbon atom in ortho-position to Y, and R and R' together may complete a heterocyclic nucleus, optionally substituted, e. g., by a hydroxyl or a sulpho group); and Z and Z' are hydrogen or alkyl or substituted alkyl.

The developing agents according to formula (II) may be prepared, for instance, by reaction of a compound of the formula Y-Ar-NH₂ with an aldehyde or a ketone (ZZ'CO) and a bisulphite or sulphur dioxide.

These developing agents may be used for the production of black-and-white images, especially fine-grain

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images, or of color images. In the latter case, the presence of a color coupler either in the photographic material or in the developing solution is required.

The developing agents according to our invention produce on color development the same dyestuff as the developing agents of the formula Y-Ar-NH₂ since the group CZZ'SO₃M is split off. This fact facilitates considerably the replacement of compounds of the formula Y-Ar-NH₂ by corresponding compounds of Formula II.

The latter compounds, except for those derived from acroleine, are but little or not at all allergic to the skin. Also, developing solutions containing the developing agents of our invention do not darken under the influence of air.

Developing solutions containing our developing agents should also contain the usual ingredients such as an alkaline substance, and a restrainer such as potassium bromide. The addition of a sulphite is generally not required, although it may be used in some cases, but further substances may be added, such as a further developing agent, a buffering agent as, for instance, disodium hydrogen phosphate, and an emulsion hardener as, for instance, formaldehyde. The solution may be composed before use from two or more solutions, concentrated solutions, or powders.

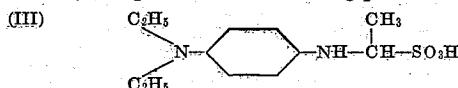
The developing agents may be added to the photographic material as well. In this case, the material may be developed, after exposure, in an alkaline solution.

Our developing agents may be used, as is known, for producing a negative or a reversed image from an exposed color photographic material by color development. The silver image simultaneously formed with the dye image as well as the negative silver image in a reversal process may be eliminated.

The following examples serve to illustrate this invention, without limiting, however, the scope thereof.

Example 1

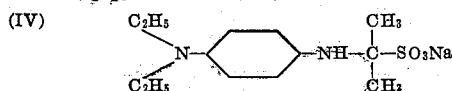
To a solution of 4.4 g. acetaldehyde in 40 ccm. water are added, while cooling in ice, 20 g. sodium bisulphite. After also adding 16.4 g. N,N-diethyl-p-phenylene diamine, the mixture is heated on the water bath for 13 minutes, while shaking. After cooling, the crystals formed are sucked off and purified by crystallization from water. Melting point: 143–145° C. The product obtained corresponds to the following probable formula:



Alternately, 150 ccm. water are saturated with SO₂ at room temperature and 16.4 g. N,N-diethyl-p-phenylene diamine are dissolved therein. By adding 4.4 g. acetaldehyde, the mixture becomes hot. After cooling, the precipitate formed is sucked off and washed with ethanol. Melting point: 140–143° C. After recrystallization from water, the melting point is 143–145° C. The product obtained likewise corresponds to the probable Formula III.

Example 2

To a solution of 25 g. sodium bisulphite and 11.6 g. acetone in 60 ccm. water are added 37.5 g. N,N-diethyl-p-phenylene diamine. This mixture is shaken at 20° C. until a crystalline precipitate is formed and the N,N-diethyl-p-phenylene diamine is almost dissolved, whereafter the crystals formed are sucked off. The precipitate is thoroughly washed with acetone. Melting point: above 330° C. The product obtained corresponds to the following probable formula:

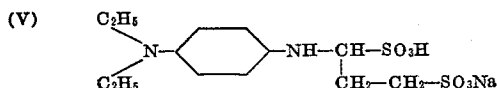


Example 3

To a solution of 62 g. bisulphite in 200 ccm. water, contained in a flask with reflux condenser, are added 11.2 g. acroleine, while shaking. While the shaking is continued, 33 g. N,N-diethyl-p-phenylene diamine are added and the mixture is heated for 10 minutes

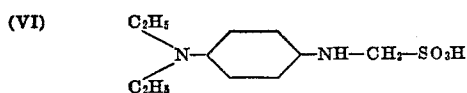
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on the water bath. After cooling, the crystals formed are sucked off and purified by crystallization from an ethanol-water mixture 1/1. Melting point: 166–168° C. The product obtained corresponds to the following probable formula:



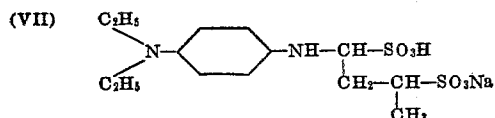
Example 4

To a solution of 15 g. sodium bisulphite in 30 ccm. water and 10 ccm. of an aqueous solution of formaldehyde 30% are added 16.5 g. N:N-diethyl-p-phenylene diamine, while shaking. The mixture is heated for 5 minutes on the water bath. After cooling, the crystals formed are sucked off and purified by crystallization from an ethanol-water mixture 1/1. Melting point: 190–193° C. The product obtained corresponds to the following probable formula:



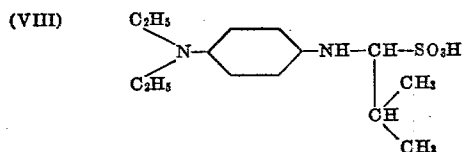
Example 5

11.5 g. dry sodium bisulphite and 3.5 g. croton aldehyde are dissolved in 40 ccm. water by heating. After cooling, the solution is shaken with 9.9 g. N:N-diethyl-p-phenylene diamine for 4 hours and next concentrated in vacuo. The precipitate formed is sucked off and washed with acetone. Melting point: above 330° C. The product obtained corresponds to the following probable formula:



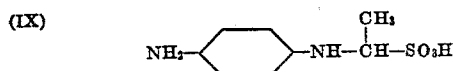
Example 6

15.9 g. dry sodium bisulphite and 11 g. iso-butyric aldehyde are dissolved in 40 ccm. water by heating on the water bath. To this solution is added a solution of 32 g. N:N-diethyl-p-phenylene diamine sulphate in 100 ccm. water, and the whole is heated for 2 hours on the water bath. Crystals form which after cooling are sucked off and recrystallized from water. Melting point: 136–139° C. The product obtained corresponds to the following probable formula:



Example 7

To a solution of 10.4 g. dry sodium bisulphite and 4.4 g. acetaldehyde in 100 ccm. water are added 13 g. p-phenylene diamine. Upon shaking, the p-phenylene diamine first dissolves. After about 15 minutes, a precipitate is formed which is sucked off and recrystallized from an aqueous solution of ethanol 50%. Melting point: 142–143° C. The product obtained corresponds to the following probable formula:

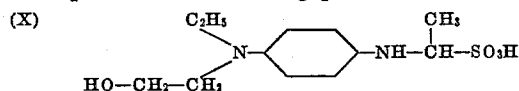


Example 8

2.2 g. paraldehyde are dissolved in a solution of 5.2 g. dry sodium bisulphite in 30 ccm. water. After heating for 2 hours on the water bath with 11.5 g. N-ethyl-N-beta-hydroxy ethyl-p-phenylene diamine sulphate, and after cooling, the precipitate formed is sucked off, washed with acetone and recrystallized from water.

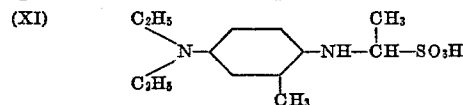
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Melting point: 128–130° C. The product obtained corresponds to the following probable formula:



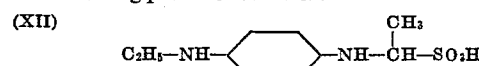
Example 9

5.2 g. dry sodium bisulphite and 2.2 g. paraldehyde are dissolved in 30 ccm. water and heated for 2 hours on the water bath with 10.7 g. 2-amino-5-diethylaminotoluene hydrochloride. After cooling, the precipitate formed is sucked off and washed with acetone. Melting point: 135–138° C. The product obtained corresponds to the following probable formula:



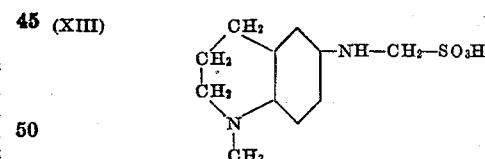
Example 10

5.2 g. dry sodium bisulphite and 2.2 g. paraldehyde are dissolved in 30 ccm. water and heated for 2 hours on the water bath with 9.2 g. mono-ethyl-p-phenylene diamine sulphate. After cooling, the precipitate formed is sucked off and washed with acetone. Melting point: 151–153° C. The product obtained corresponds to the following probable formula:



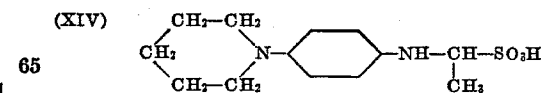
Example 11

2.8 g. dry sodium bisulphite dissolved in 10 ccm. water and 2.5 ccm. of an aqueous solution of formaldehyde 36% are heated for 15 minutes at 40–50° C. with 3.5 g. sodium bicarbonate and 5.4 g. N-methyl-6-amino-tetra-hydroquinoline-oxalate in 90 ccm. water. The precipitate formed is sucked off and recrystallized from diluted alcohol. Melting point: 149–150° C. The product obtained corresponds to the following probable formula:



Example 12

0.5 g. paraldehyde and 1.25 g. dry sodium bisulphite are dissolved in 10 ccm. water and heated for 2 hours on the water bath with 2.1 g. N-(p-aminophenyl)-piperidine. After cooling, the precipitate formed is sucked off and recrystallized from water. Melting point: 139° C. The product obtained corresponds to the following probable formula:



Example 13

A silver bromo-iodide gelatine emulsion layer is developed in a bath of the following composition:

	G.
A developing substance according to Examples 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12	5
Metol (methyl-para-aminophenol-sulphate)	2
Sodium sulphite (cryst.)	120
Trisodium phosphate	3.5
Potassium bromide	1
Water to 1000 ccm.	

is washed, fixed, washed again and dried. A fine-grain black-and-white image is obtained. Besides gelatine, also collodion, a water-permeable cellulose ester, or another water-permeable synthetic resin may be used as a binding agent for the silver halide.

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Example 14

A silver halide gelatine emulsion layer, after exposure, is developed in a bath of the following composition:

- (A) A color developing substance according to Examples 1, 2, 3, 4, 5, 6, 8, 9, 10, 11 or 12 ----- g ----- 5
Sodium sulphite (cryst.) ----- g ----- 10
Sodium carbonate (cryst.) ----- g ----- 100
Water to 1000 ccm. ----- 10
- (B) 1-phenyl-3-(m-nitrophenyl)-5-pyrazolone --g-- 1
Alcohol ----- ccm-- 20
(Before use, B is added to A.)

is washed, freed from silver with a potassium ferricyanide solution, washed again, fixed, washed for a third time and dried. A pure magenta image is obtained.

Example 15

A multi-layer material comprising:

- (a) A support as, for instance, glass, paper or film;
(b) A silver bromo-iodide emulsion layer containing for 1 kg. emulsion 30 mg. {2-[3-allyl-5-(3-ethylbenz-thiazolylidene-2-ethylidene)-thiazolone-4]} {2-(3-ethyl-4:5-diphenyl-thiazol)} -monomethinecyanine-iodide and 8 g. 1-hydroxy-4-sulpho-2-naphthoic acid octadecyl amide;
(c) A silver bromo-iodide emulsion layer containing for 1 kg. emulsion 30 mg. di[2-(3-ethyl-5-phenylbenz-oxazol)1 -beta-ethyl-trimethine cyanine-ethyl sulphate and 8 g. 1-(p-sulphophenyl)-3-m-stearoyl-amino)-phenyl-5-pyrazolone;
(d) A colloidal silver intermediate layer; and
(e) A silver bromo-iodide emulsion layer containing for 1 kg. emulsion 10 g. [(m-stearoylamino)-benzoyl] aceto-(3:5-dicarboxy)-anilide

is exposed, developed in a metolhydroquinone developer, washed, exposed to white light, developed in a bath composed as follows:

- G.
A color developing substance according to Examples 1, 2, 3, 4, 5, 6, 8, 9, 10, 11 or 12 ----- 4
Sodium sulphite (cryst.) ----- 5
Potassium carbonate ----- 75
Potassium bromide ----- 2.5
Water to 1000 ccm.

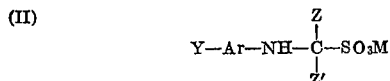
washed again, freed from silver with a potassium ferricyanide solution, washed once more, fixed, finally washed and dried. A positive color image is obtained.

Example 16

A photographic multi-layer material as described in Example 15, containing sensitizers and color couplers fast to diffusion, may after exposure be directly developed in the above mentioned color developing bath and further treated as in Example 15. The negative color image obtained may be copied upon similar multi-layer material, and by treatment in a like manner as to obtain the negative, a positive copy image is obtained.

We claim:

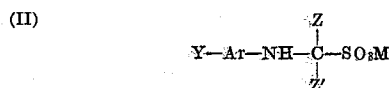
1. Process for developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



wherein M is a member selected from the group consisting of hydrogen and a water-soluble salt-forming cation; Ar is p-phenylene; Y is a substituent of Ar in para-position to the nitrogen atom, selected from the group consisting of an amino group substituted by a hydrocarbon radical, an amino group substituted by two hydrocarbon radicals, an amino group substituted by two substituents completing together a heterocyclic radical, and an amino group substituted by a substituent linked to the carbon atom in ortho-position to Y; and Z and Z' are members selected from the group consisting of hydrogen and alkyl.

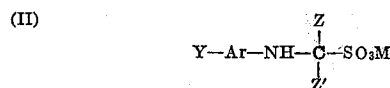
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2. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



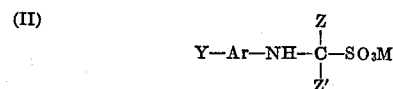
wherein M is a member selected from the group consisting of hydrogen and a water-soluble salt-forming cation; Ar is p-phenylene; Y is a substituent of Ar in para-position to the nitrogen atom, selected from the group consisting of an amino group substituted by a hydrocarbon radical, an amino group substituted by two hydrocarbon radicals, an amino group substituted by two substituents completing together a heterocyclic radical, and an amino group substituted by a substituent linked to the carbon atom in ortho-position to Y; and Z and Z' are members selected from the group consisting of hydrogen and alkyl.

3. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



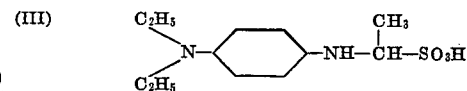
wherein M is a member selected from the group consisting of hydrogen and a water-soluble salt-forming cation; Ar is p-phenylene; Y is a para-substituent of Ar consisting of an amino group substituted by a substituent linked to the carbon atom in ortho-position to Y; and Z and Z' are members selected from the group consisting of hydrogen and alkyl.

4. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:

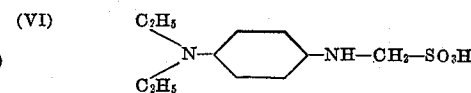


wherein M is a member selected from the group consisting of hydrogen and a water-soluble salt-forming cation; Ar is p-phenylene; Y is a substituent of Ar in para-position to the nitrogen atom, selected from the group consisting of an amino group substituted by a hydrocarbon radical, an amino group substituted by two hydrocarbon radicals, and an amino group substituted by two substituents completing together a heterocyclic radical; and Z and Z' are members selected from the group consisting of hydrogen and alkyl.

5. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



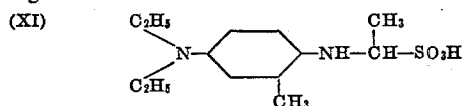
6. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



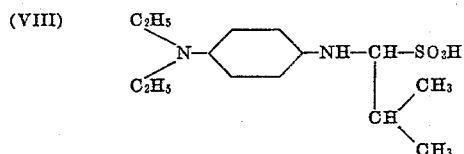
7. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such

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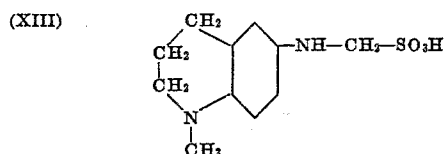
layer with a developer containing a compound according to the formula:



8. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



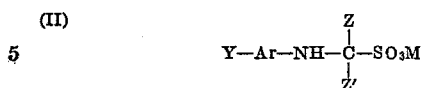
9. Process for forming a colored image by developing a reducible silver salt image in a photographic silver halide emulsion layer, which comprises treating such layer with a developer containing a compound according to the formula:



10. A photographic developing solution containing an alkaline substance, a restrainer, a preserving agent, and

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as a silver halide agent a compound according to the formula:



wherein M is a member selected from the group consisting of hydrogen and a water-soluble salt-forming cation; Ar is p-phenylene; Y is a substituent of Ar in para-position to the nitrogen atom, selected from the group consisting of an amino group substituted by a hydrocarbon radical, an amino group substituted by two hydrocarbon radicals, an amino group substituted by two substituents completing together a heterocyclic radical, and an amino group substituted by a substituent linked to the carbon atom in ortho-position to Y; and Z and Z' are members selected from the group consisting of hydrogen and alkyl.

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