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[54] TETRA-ALKYL P-PHENYLENE DIAMINE  
WITH AROMATIC PRIMARY AMINO  
COLOR DEVELOPING AGENT

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[58] Field of Search ..... 96/66 R, 66.3, 55

[56] References Cited

UNITED STATES PATENTS

3,265,502 8/1966 Willems et al. .... 96/66 R  
3,615,525 10/1971 Willems ..... 96/66 R

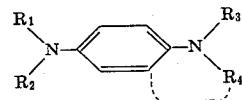
FOREIGN PATENTS OR APPLICATIONS

1,149,794 4/1969 Great Britain ..... 96/66 R

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Attorney—Alfred W. Breiner

[57] ABSTRACT

A photographic colour developing composition for silver halide material is described which comprises besides the aromatic primary amino colour developing agent a tetraalkyl p-phenylene diamine compound of the formula :



wherein

each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> is C<sub>1</sub>—C<sub>6</sub> alkyl or R<sub>1</sub> together with R<sub>2</sub> represent the atoms necessary to close a pyrrolidine ring, and

R<sub>4</sub> is C<sub>1</sub>—C<sub>6</sub> alkyl or ethylene or propylene linked to the C-atom of the phenylene ring in ortho position to the amino group carrying the R<sub>4</sub>-substituent, one of R<sub>1</sub>—R<sub>4</sub> being a C<sub>2</sub>—C<sub>6</sub> alkyl group carrying a solubilizing group. The tetraalkyl p-phenylene diamine compound increases the activity of the colour developing agent without effecting to a noteworthy extent the fog and gradation of the silver halide material.

6 Claims, No Drawings

**TETRA-ALKYL P-PHENYLENE DIAMINE WITH  
AROMATIC PRIMARY AMINO COLOR  
DEVELOPING AGENT**

The present invention relates to a process for the colour development of photographic silver halide materials containing exposed silver halide and to developing compositions used therein.

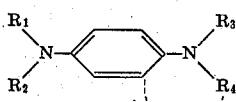
It is known that the developing activity of a developing solution containing a mixture of several developing substances can be higher than the sum of the developing activities of the separate developing solutions of each of these developing substances used in the same concentration as in the solution of that mixture. This phenomenon is called superadditive development.

The most common superadditive developing combinations for the development of exposed black-and-white photographic silver halide elements are p-monomethylaminophenol together with hydroquinone and 1-phenyl-3-pyrazolidinone together with hydroquinone. It is further known that certain p-phenylene diamine derivatives have a superadditive development effect when used together with hydroquinone.

It is known that for the production of a photographic colour image in a light-sensitive silver halide layer, the exposed silver halide is developed to a silver image by means of an aromatic primary amino developing agent in the presence of a colour coupler which reacts with the oxidized developing agent to form a dyestuff on the areas corresponding to the silver image. In J.Phot.Sci. 11 (1963) 136-139, it has been shown that 1-phenyl-3-pyrazolidinone and p-monomethylaminophenol also increase the activity of these aromatic primary amino colour developing agents, the first compound being the most active of the two. As is known from French Pat. No. 1,283,420 other p-aminophenol derivatives also activate colour development by means of N,N-dialkyl-p-phenylene diamine developing agents.

Though 1-phenyl-3-pyrazolidinone has a high development activating effect it shows the disadvantage of strongly increasing the fog and reducing the gradation; this also applies to the p-aminophenol compounds.

It has now been found that the activity of aromatic primary amino colour developing agents, used for the development of photographic silver halide elements in the presence of colour forming couplers can be increased without effecting the fog and gradation to a noteworthy extent by means of non colour forming tetra-alkyl-p-phenylene diamine derivatives corresponding to the following general formula :



wherein :

each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl, or R<sub>1</sub> together with R<sub>2</sub> represents the atoms necessary to close a pyrrolidine ring, and

R<sub>4</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or ethylene or propylene linked to the C-atom of the phenylene ring in ortho-position to the amino group carrying the R<sub>4</sub>-substituent,

one of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> being a C<sub>2</sub>-C<sub>6</sub> alkyl group carrying a solubilizing group which includes such groups

as carboxyl, sulpho, ionizable sulphonamido and hydroxyl.

Therefore, in accordance with the present invention photographic developing compositions for developing, in the presence of a colour forming coupler, an exposed silver halide emulsion layer of a photographic element are provided which comprise, in addition to an aromatic primary amino colour developing agent, a tetraalkyl-p-phenylene diamine derivative as represented by the above general formula.

The present invention also provides a process for the production of photographic colour images which comprises treating a photographic material having a layer containing developable silver halide with an aqueous alkaline solution in the presence of a colour forming coupler, an aromatic primary amino colour developing agent and a tetraalkyl-p-phenylene diamine derivative corresponding to the above general formula.

The ratio of tetraalkyl-p-phenylene diamine derivative corresponding to the above general formula to aromatic primary amino colour developing agent used in accordance with the present invention, can vary within wide limits. A strong superadditive effect is obtained already with a ratio of 50 mg of tetraalkyl-p-phenylene diamine derivative to 3 g of colour developing agent. Generally the amount of the tetraalkyl-p-phenylenediamine derivative is comprised between 10 mg and 1 g per litre.

Representative examples of compounds corresponding to the above general formula are :

1. N,N-diethyl-N'-2-hydroxyethyl-N'-ethyl-p-phenylenediamine disulphate
2. N,N-diethyl-N'-4-sulphobutyl-N'-ethyl-p-phenylenediamine hydrochloride
3. N,N-diethyl-N'-3-sulphopropyl-N'-propyl-p-phenylenediamine
4. N,N-diethyl-N'-3-carboxypropyl-N'-ethyl-p-phenylenediamine dihydrochloride
5. 1-(4-sulphobutyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline
6. 1-(2-hydroxyethyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride
7. 1-ethyl-6-(N-ethyl-N-3-sulphopropylamino)-1,2,3,4-tetrahydroquinoline
8. 1-(3-sulphopropyl)-6-(N-ethyl-N-methylamino)-1,2,3,4-tetrahydroquinoline
9. 1-(3-carboxypropyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline
10. 1-( $\beta$ -methylsulphonamidoethyl)-6-diethylamino-1,2,3,4-tetrahydroquinoline dihydrochloride.
11. 1-(p-N-ethyl-N-sulphopropylamino-phenyl)-pyrrolidine hydrochloride.

The above compounds can be prepared as illustrated in United Kingdom Pat. Nos. 989,383 and 1,191,535.

The tetraalkyl-p-phenylene diamine compounds of the above general formula can be used in processes wherein the colour-forming couplers are dissolved in the developer as well as in processes wherein the colour-forming couplers are incorporated in the photographic element. They can be used in negative processes as well as in reversal processes.

The tetraalkyl-p-phenylene diamine compounds of the above general formula are effective not only when used in the colour developing solution comprising the aromatic primary amino colour developing agent but also when used in a supplemental alkaline treating solu-

tion included in the colour processing directly after the colour development step.

The compounds corresponding to the above general formula are used to advantage in producing colour images using any of the well known aromatic primary amino colour developing agents more particularly N,N-dialkyl-p-phenylene diamines and derivatives thereof, e.g., the toluene analogues. All of these colour developing agents have an unsubstituted amino group which enables the oxidation product of the developing agent to couple with the colour forming couplers to form a dye image. Typical examples of aromatic primary amino colour developing agents are : N,N-diethyl-p-phenylene diamine, 2-amino-5-diethylaminotoluene, N-butyl-N-sulphobutyl-p-phenylene diamine, 2-amino-5-[N-ethyl-N-( $\beta$ -methylsulphonamido)ethyl] aminotoluene, N-ethyl-N- $\beta$ -hydroxyethyl-p-phenylene diamine, etc. These developing agents are usually used in the salt form such as the hydrochloride or sulphate.

Alkali, alkali metal sulphites, alkali metal halides, thickening agents such as carboxymethyl cellulose for making viscous developers, and any of the other additives included in colour developing solutions such as hydroxylamine and derivatives such as N,N-diethylhydroxylamine may be used in the colour developers employed in the colour development process of the present invention.

In the subtractive three-colour photography usually a photographic multilayer colour element is used containing a red-sensitized, a green-sensitized and a blue-sensitive silver halide emulsion layer wherein on colour development, by the use of appropriate colour couplers, a cyan, magenta and yellow dyestuff image are formed, respectively. Other multicolour elements have the three differently sensitized silver halide grains dispersed in a single emulsion layer, e.g., an emulsion layer of the mixed packet type as described in U.S. Pat. No. 2,698,794 or an emulsion layer of the mixed grain type as described in U.S. Pat. No. 2,592,243.

As stated above, the colour forming couplers may be soluble colour couplers used in the colour developer or non-diffusible colour couplers incorporated in the photographic element. Usually naphtholic or phenolic couplers are used to form the cyan dye image, indazolone or pyrazolone couplers to form the magenta dye image, and open chain ketomethylene couplers to form the yellow dye image.

The compounds corresponding to the above general formula may also be used to activate colour development, by means of aromatic primary amino colour developing agents, of radiographic colour materials, for example of the kind described in U.S. Pat. application Ser. Nos. 852,236 and 852,246. In U.S. Pat. application Ser. No. 852,236 a method is described and claimed for the production of colour radiographs according to which in a recording material comprising one or more silver halide emulsions a developable silver image is formed by means of directly or indirectly recorded penetrating radiation the said material being processed in such a way that at least two images of contrasting colour and of opposite gradation are obtained. In U.S. Pat. application Ser. No. 852,246 a method is described and claimed according to which monochromic radiographic images are produced, optionally together with a silver image, thus offering more visual retrieval of in-

formation than corresponding black-and-white radiographic images.

For the purpose of accelerating the colour development of photographic elements by means of the aromatic primary amino colour developing agent together with a tetraalkyl-p-phenylene diamine derivative of the above formula, the said elements can be developed in the presence of development accelerators. These development accelerators can be used either in a silver halide emulsion layer of the photographic element or in the developing composition itself. They include alkylene oxide compounds of various types for example alkylene oxide condensation products or polymers as described in U.S. Pat. Nos. 1,970,578; 2,240,472; 2,423,549; 2,441,389; 2,531,832 and 2,533,990 and in United Kingdom Pat. Specification Nos. 920,637; 940,051; 945,340; 991,608 and 1,015,023. Other development accelerating compounds are onium and polyonium compounds preferably of the ammonium, sulphonium and phosphonium type, including onium polyoxyalkylene salts especially polyoxyalkylene bis-pyridinium salts examples of which can be found in U.S. Pat. No. 2,944,900, etc.

The following examples illustrate the present invention.

#### EXAMPLE 1

An exposed multilayer colour photographic negative film carrying three differently sensitized emulsion layers containing cyan, magenta, and yellow colour formers respectively was developed for 6 min. at 24°C in a colour developer, made up according to the following recipe :

water — 900 ml  
sodium hexametaphosphate — 1 g  
sodium sulphite (anh.) — 4 g  
N,N-diethyl-p-phenylene diamine hydrochloride — 2.7 g  
sodium carbonate (anh.) — 25 g  
sodium hydroxide — 0.5 g  
potassium bromide — 2.2 g  
hydroxylamine hydrochloride — 1.2 g  
water to make — 1000 ml (pH : 10.7)

On completion of the development step the photographic material was rinsed and transferred for 2 min. to an acid hardening fixer of the following composition :

water — 800 ml  
sodium thiosulphate (anh.) — 200 g  
sodium bisulphite — 12 g  
glacial acetic acid — 12 ml  
borax — 20 g  
potassium alum — 15 g  
water to make — 1,000 ml (pH : 3.9)

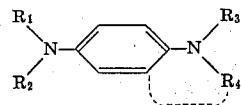
The photographic material was then washed and transferred for 3 min. to a silver bleach bath of the following composition :

water — 800 ml  
potassium bromide — 15 g  
potassium ferricyanide — 75 g  
potassium aluminium sulphate — 15 g  
sodium acetate — 5 g  
acetic acid — 10 g  
water to make — 1000 ml (pH : 3.65)

After having rinsed the material it was treated again for 2 min. in the above fixing solution whereupon it was finally washed and dried.

The sensitometric results obtained are listed in the following table as compared with the results obtained when one of the compounds listed in the table below are added to the colour developer in an amount of 0.2 millimole per litre.

diamine compound corresponding to the general formula:



TABLE

Compound added	Blue-sensitive layer			Green-sensitized layer			Red-sensitized layer		
	Fog	Gradation	Rel. speed*	Fog	Gradation	Rel. speed	Fog	Gradation	Rel. speed
None	0.14	0.48	100	0.16	0.49	100	0.09	0.42	100
Compound 2	0.16	0.55	155	0.17	0.49	155	0.09	0.44	183
Compound 3	0.14	0.58	145	0.16	0.48	142	0.09	0.46	155
Compound 4	0.15	0.67	148	0.17	0.53	146	0.09	0.50	175

\*The values given for the speed are relative values. The speed obtained with the comparison developer comprising no superadditive developing compound is given a value of 100.

The above results show that the compounds corresponding to the above general formula accelerate development and, with approximately the same fog-value, increase the speed without adversely affecting the gradation.

The same favourable results are obtained when instead of adding the tetraalkyl-p-phenylene diamine derivatives to the developing solution the material was treated after development with an alkaline solution (pH : 10.7) of these compounds.

#### EXAMPLE 2

A radiographic colour material comprising a polyethylene terephthalate support and on both sides thereof a high-speed gelatin silver bromoiodide emulsion comprising a colour coupler, was exposed through a wedge and colour processed to yield a coloured wedge print. Development occurred by treatment of the exposed material for 27 sec. at 40°C in a colour developer comprising N-ethyl-N-β-hydroxyethyl-p-phenylene diamine as colour developing agent and one of the superadditive black-and-white developing agents listed in the table below.

The sensitometric results obtained are listed in the table below. The values given for the speed are relative values measured at density 1 above fog. The value of 100 was given to the speed of the material developed in a developer comprising no superadditive developing agent. The values given for the gradation were measured behind a red filter between density 0.25 and 2.0 above the fog value.

TABLE

Compound added per litre	Fog	Gradation	Relative speed
none	0.16	2.45	100
0.62 mmole of 1-phenyl-3-pyrazolidinone	0.80	3.07	235
0.62 mmole of compound 2	0.24	2.73	135
0.62 mmole of compound 3	0.25	2.67	135

The above results show that under these severe circumstances of rapid development at increased temperature the compounds corresponding to the above general formula still activate development without increasing fog to such undesirable extent as 1-phenyl-3-pyrazolidinone.

We claim :

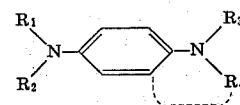
1. A photographic developer composition for use in the colour development of silver halide photographic material which comprises an aromatic primary amino colour developing agent and a tetraalkyl p-phenylene

wherein:

each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or R<sub>1</sub> together with R<sub>2</sub> represents the atoms necessary to 20 close a pyrrolidine ring, and R<sub>4</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or ethylene or propylene linked to the C-atom of the phenylene ring in ortho position to the amino group carrying the R<sub>4</sub> substituent, one of R<sub>1</sub>-R<sub>4</sub> being a C<sub>2</sub>-C<sub>6</sub> alkyl group carrying a solubilizing group which is a member of the group consisting of carboxyl, sulpho, ionizable sulphonamide, and hydroxyl.

2. A photographic developer composition according to claim 1, wherein the aromatic primary amino colour 30 developing agent is a N,N-dialkyl-p-phenylene diamine or toluene analog thereof.

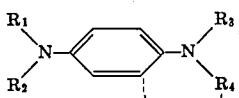
3. A process of producing photographic colour images which comprises treating a developable silver halide emulsion layer in the presence of a colour coupler 35 with a developer composition which comprises an aromatic primary amino colour developing agent and a tetraalkyl p-phenylene diamine compound corresponding to the general formula:



wherein:

each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or R<sub>1</sub> together with R<sub>2</sub> represents the atoms necessary to 50 close a pyrrolidine ring, and R<sub>4</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or ethylene or propylene linked to the C-atom of the phenylene ring in ortho position to the amino group carrying the R<sub>4</sub> substituent, one of R<sub>1</sub>-R<sub>4</sub> being a C<sub>2</sub>-C<sub>6</sub> alkyl group carrying a solubilizing group which is a member of the group consisting of carboxyl, sulpho, ionizable sulphonamide, and hydroxyl.

4. A process according to claim 3, wherein said colour coupler is present in the said emulsion layer. 60 5. A process of producing photographic colour images which comprises treating a developable silver halide emulsion layer in the presence of a colour coupler with a colour developing composition comprising an aromatic primary amino colour developing agent and then treating the developed emulsion layer with an alkaline composition comprising a tetraalkyl-p-phenylene diamine compound corresponding to the formula:



wherein:

each of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or R<sub>1</sub> together with R<sub>2</sub> represents the atoms necessary to close a pyrrolidine ring, and R<sub>4</sub> stands for C<sub>1</sub>-C<sub>6</sub> alkyl or ethylene or propylene linked to the C-atom of the phenylene ring in ortho position to the amino group 10

carrying the R<sub>4</sub> substituent, one of R<sub>1</sub>-R<sub>4</sub> being a C<sub>2</sub>-C<sub>6</sub> alkyl group carrying a solubilizing group which is a member of the group consisting of carboxyl, sulpho, ionizable sulphonamide, and hydroxyl.

5. A process according to claim 5, wherein the aromatic primary amino colour developing agent is a N-N-dialkyl-p-phenylene diamine or toluene analog thereof.

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