United States Patent

[11] **3,622,629**

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Wilmington, Del.
Continuation-in-part of application Ser. No. 663,494, Aug. 28, 1967. This application June 19, 1968, Ser. No. 738,109

[54] N-(HYDROXY-AMINOBENZYL)-3-HYDROXY-ANILINE COMPOUNDS

7 Claims, No Drawings

[52] **U.S. Cl.** .... **260/570 AB,**
96/66 R, 96/66 HD, 260/288 R, 260/296 R,
260/304, 260/309.2, 260/310 A, 260/326.5 J,
260/519, 260/567.6 M, 260/570.5 R, 260/570.5 P,
260/570.9, 260/622 R
[51] **Int. Cl.** **C07c 91/28,**
C07c 91/42, F231 17/02
[50] **Field of Search** 260/570,
570.9, 519, 570.5

[56] **References Cited**

UNITED STATES PATENTS

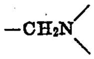
3,091,530	5/1963	Green et al.	260/570.9 X
3,311,660	3/1967	Krimm et al.	260/570
3,359,317	12/1967	Krimm et al.	260/570 X

OTHER REFERENCES

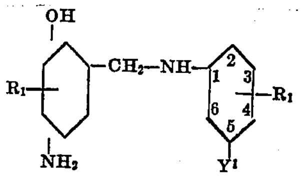
Agarwal et al., Chemical Abstracts, Volume 55, pp. 27206–27207 (1961).

Primary Examiner—Floyd D. Higel
Attorney—Lynn Barratt Morris

ABSTRACT: Developer-coupler compounds having within the same molecule a p-aminophenol nucleus capable of developing a silver halide image and a separate dye forming nucleus capable of dye-coupling in situ during development of latent silver halide images to form a colored dye, e.g., a quinoneimine or azomethine dye image. The silver image and the dye image provide a combined image of high total maximum density with a minimum of initial silver halide. The p-aminophenol developer nucleus and coupler nucleus of the molecule are linked through a position ortho to the hydroxyl group of said p-aminophenol nucleus through a radical



wherein a free bond attached to CH_2 N are attached to cyclic carbon atoms. A representative and preferred compound has the formula



wherein the rings are benzene rings, R_1 is H, alkyl or one-four carbons, C1, Br, or —COOH, and Y' is —OH or $—NH_2$, and at least one of the coupling positions 2 and 4 is a free coupling position. Bis compounds containing a nuclei, as recited, are comprehended. The developer-coupler compounds are useful also in radiation-sensitive silver halide layers.

N-(HYDROXY-AMINOBENZYL)-3-HYDROXY-ANILINE COMPOUNDS

This application is a continuation-in-part of my Application Ser. No. 663,494, filed Aug. 28, 1967 abandoned Sept. 22, 1969.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention concerns novel compounds in which a photographic developer portion of the molecule is connected through a cyclic carbon atom to a dye-coupling portion of the molecule. The invention also pertains to developer solutions and colloid-silver halide photographic layers or elements containing these novel compounds as well as processes for developing photographic elements in the presence of these compounds in order to obtain images comprised of both reduced silver and coupled dye.

2. Description of the Prior Art

It has long been known that some silver halide developing agents, e.g., pyrogallol and catechol but also hydroquinone and aminophenols deposit an additional colored image along with the silver image. This so-called residual image, which consists chiefly of quinoid oxidation products of the developer substance, can be made more visible by converting the silver to a silver salt with a mild oxidizing agent and fixing in the usual way. The black-and-white developers mentioned indeed lead to silver images with high density but the colored image is not pronounced. It is known that the colored image can be enhanced by reconverting the image silver into a light-sensitive silver compound and exposing and developing the silver compound. This can be repeated until the dye density is increased to a desired higher density. However, this process is tedious and uneconomical and has found no application in commercial practice.

The difficulty soluble, quinoid developer oxidation products form only in the absence of sodium sulfite, whereas, in the presence of the latter, soluble sulfonic acids result. Also, sulfite-free developer solutions are completely unstable and cannot be used for practical purposes.

Moreover, it is known that p-phenylenediamine and its derivatives form oxidation products in the reduction of silver halides that form dyes with suitable coupling components, especially phenols, naphthols or ketomethylene compounds, which precipitate simultaneously with the reduced silver. After removal of the image silver, there result pictures with one or more dye images only.

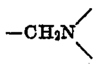
From U.S. Pat. No. 2,181,944 and the German Pat. application 57*b*, 13, H 11 099, it is known also to produce black-and-white pictures by the above process. These pictures, in which the dyes formed in developing constitute the only image, however, do not possess adequate density.

An additional process for producing black-and-white photographic images through chromogenic developing is described in German Pat. No. 1,158,836. It is indeed possible to achieve an appreciable increase in sensitivity according to this process. However, as is evident especially from the patent (last sentence of example 2), it is not possible to obtain images according to this process wherein the density is a great deal higher than that obtained with a commercial black-and-white developer.

Other references have disclosed the formation of black or dark colored dye images along with metallic silver images, but these processes have not employed compounds in which the silver halide developer and dye coupler are combined in a single molecule. In the earlier references, it has apparently not been possible to reduce substantially the amount of silver halide required to produce a given maximum density by augmenting the silver image with a dye image. According to Weber U.S. Pat. No. 2,173,739, a colored dye image which was opaque to printing light was used to augment the silver image in a negative. Although this would not have given a satisfactory image in a final positive print, it was useful in a negative trough which a positive is printed.

SUMMARY OF THE INVENTION

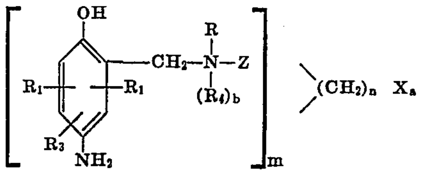
The photographic developer-coupler compounds of the invention as previously indicated comprise at least one p-aminopnenol nucleus wherein the nitrogen atom has two hydrogen atoms attached thereto, the said nucleus being linked through a



$$-CH_2N<$$

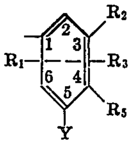
radical to a separate dye-forming nucleus capable of forming a dye, e.g., a quinoneimine (i.e., indophenol, indothiophenol, indamine or indoaniline) or azomethine dye upon development of silver halide images, the free bond attached to the CH_2 group being attached to cyclic carbon of the p-aminophenol nucleus and one free bond attached to the nitrogen atoms being attached to a cyclic carbon atom in the dye-forming nucleus.

A group of such compounds of the invention can be represented by the general formula:



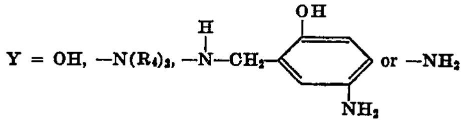
I

wherein
a, b and n=0 or 1,
m=1 when n is 0 and m=2 when n is 1,
X is a negative ion or radical of an acid, e.g., Cl
Z is

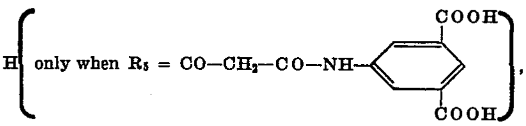


where at least one of the positions 2- and 4- is a free coupling position, e.g., an unsubstituted hydrogen atom, halogen, $-SO_3H$ or an azo group, or

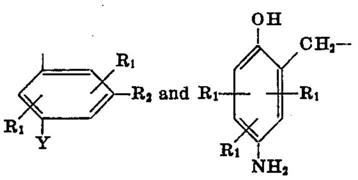
R and Z together may represent the atoms necessary to complete a 5- or 6-membered nitrogen-containing heterocyclic nucleus which may be substituted with Y, alkyl or a fused aromatic ring,



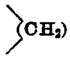
or



R=H, alkyl of one to four carbon atoms, aralkyl, carboxymethyl, unsubstituted and substituted aryl groups including

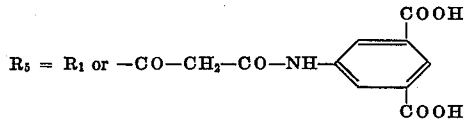


wherein
R_1=H, alkyl of one to four carbons, Cl, Br or -COOH-.
R_2=H, alkyl of one to four carbons, Cl, or Br, OH or $-NH_2$,
R_3=a bond to



when n=1 or R_1 when n=0,

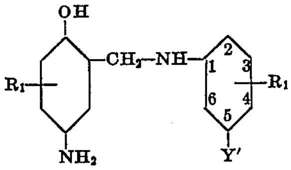
R_4=alkyl of one to four carbon atoms



and

Y is the same as in formula I.

In an important aspect of the invention, compounds falling under formula I but which form brownish-black to black images can be represented by the formula:

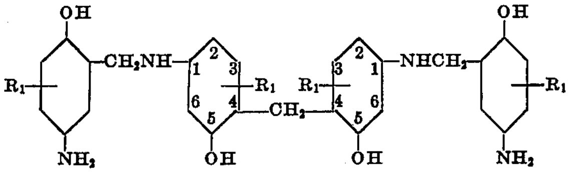


II

wherein: R_1 is H, alkyl of one to four carbon atoms, Cl, Br or COOH, and

Y' is OH or $-NH_2$ and at least one of positions 2 and 4 is a free coupling position.

In another specific aspect of the invention the methylene bis compounds falling under formula I but which also form brownish-black to black dyes can be represented by the formula:



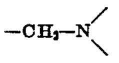
III

wherein

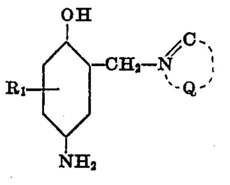
R_1 is H, alkyl of one to four carbon atoms, Cl, Br or COOH, and position 2- is a free coupling position.

Suitable alkyl radicals R_1, R_2, and R_4 for the formulas hereof are methyl, ethyl, isopropyl and butyl.

In another specific aspect of the invention the N atom in the linking radical



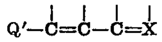
is part of a heterocyclic 5- to 6-membered ring having carbon and nitrogen atoms in the ring. These compounds result in yellow, orange, magneta, cyan etc., dye images and these compounds can be represented by the following formula:



IV

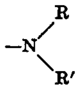
wherein Q represents the atoms necessary to complete a 5- or 6-membered heterocyclic nucleus containing a group capable of coupling to form a quinoneimine dye and R_1 is H, alkyl of one to four carbon atoms, Cl,

In the compounds of the foregoing formulas, the dye-forming nucleus may have a dye structure that may be represented by the formula

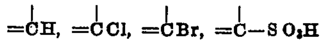


$$Q'-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{X}$$

where Q' is —OH or



; wherein R and R' is H or alkyl of one to four carbons, e.g., CH_3, C_2H_5, C_3H_7 and C_4H_9, and X, in the case of —OH containing compounds, is



$$=\overset{|}{C}H,\ =\overset{|}{C}Cl,\ =\overset{|}{C}Br,\ =\overset{|}{C}-SO_3H$$

or

$$=\overset{|}{N}$$

which is a general structure in the enol form.

The invention also relates to gelatino-silver halide photographic elements containing the novel developer-coupler compounds of the above formulas. The invention also relates to processes for developing photographic elements in the presence of the developer-coupler compounds, 1, 2 or more of the compounds being either in the emulsion or in a developer solution. By such development there are obtained images comprised of both reduced silver and coupled dyes. These images are additive in density and thus provide a very high density for a given quantity of silver halide in the photographic element. The useful dyes should have a very dark color, preferably black or blue-black, and a high extinction coefficient.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The novel developer-coupler compounds of the invention can be made in accordance with this invention by condensation. A typical compound, N-(2-hydroxy-5-aminobenzyl)-3-hydroxyaniline, is synthesized by reacting p-nitrophenol with methylal and concentrated hydrogen chloride, in the presence of concentrated sulfuric acid, to form 2-hydroxy-5-nitrobenzyl chloride. The product is then condensed with 3-aminophenol and the nitro group of this product reduced to an amine by the action of sodium hyposulfite in alkaline solution or another suitable reducing agent to give or result in the desired compound of this invention. By using other nitrophenols including substituted p-nitrophenols and substituted aminophenols, etc., other developer-coupler compounds of the foregoing general formulas can be prepared.

Such a developer-coupler compound of 2, 3 or more compounds can be used in aqueous developer solutions as the sole type of silver halide developing agent. The developer-couplers can be used in admixture with noncoupling conventional developing agents, e.g., hydroquinone, n-methyl-p-aminophenols and 1-aryl-3-pyrazolidenes. They may be mixed with adjuvants, e.g., alkali metal and ammonium sulfites such as sodium sulfite and alkaline compounds, e.g., sodium or potassium hydroxide or carbonate, and alkali metal and ammonium halides, e.g., potassium bromide, in the development of a black-and-white halide emulsion. In the development, the exposed silver halide is reduced to metallic silver while a dark colored dye image is formed in situ. In some cases the dye image can be intensified by an after treatment with an alkaline solution, e.g., an aqueous solution of NaOH. In this process, the same molecule not only reduces the silver halide but also forms the dye image by self-coupling. By using the developer-coupler compounds of this invention, it is possible to obtain a maximum density, representing the sum of the densities of silver and dye images, with about half of the silver halide coating weight required to give this maximum density in the absence of the dye image.

The developer-coupler compounds can, alternatively, be incorporated in the gelatino-silver halide element. In this embodiment, the exposed element is simply developed in an aqueous alkaline solution which activates the compounds of this invention, causing them to reduce the exposed silver halide and self-couple to form superimposed silver and dye images. Although treatment in a simple, alkaline solution causes the formation of both a silver image and a dye image, it is also possible to use a conventional photographic developer, e.g., one containing hydroquinone and p-methyl-aminophenol sulfate for generating the intensified image. The silver/dye image can also be formed by using an alkaline fixing bath in a monobath processing procedure. The novel compounds of this invention are most advantageously used in auxiliary, nonlight-sensitive layers of the gelatino-silver halide photographic element, e.g., in abrasion overcoat layers or sublayers between the light-sensitive layer and the support.

In addition to the improvement in maximum density obtained by the use of these compounds, or the possibility of attaining a given maximum density with considerably lower coating weights of silver halide, the compounds also provide improved contrast and speed (apparent).

The silver halide emulsion layers employed in combination with the compounds of this invention may contain any of the usual adjuvants such as coating aids, gelatin hardening agents, viscosity modifiers, matting agents, pigments, antihalation dyes, antifoggants, covering power agents, dispersed polymeric lattices, chemical sensitizers, spectral sensitizers, etc.

The silver halide emulsions developed in the presence of the developer-coupler compound of this invention include those employed for medical or industrial X-ray, cine, graphic arts or portrait use. The silver halide crystal may also be any one of the usual types such as silver chloride, silver bromide, silver bromochloride or silver iodobromide. Particularly useful results are obtained with high-speed medical X-ray films containing silver iodobromide crystals. Gelatin is a preferred binder for the silver halide crystals but it may be partially or completely replaced with other natural or synthetic binders as known in the art. Thus, binders used to improve covering power, e.g., dextran, dextrin, polyvinyl pyrrolidone and latices of polymers such as polyethylacrylate which are useful in improving dimensional stability have utility.

The novel developer compositions of this invention comprise the following essential ingredients:

Developer coupler compound (s)	2 to 20 g.
Alkali metal or ammonium sulfite	0 to 150 g.
An alkaline agent to adjust the pH to at least 8 and water to	1 Liter

The emulsions can be coated on any suitable support, e.g., those disclosed in Nottorf U.S. Pat. No. 3,142,568. Elements prepared from the foregoing emulsions may also comprise various auxiliary layers disclosed in the Nottorf patent, and particularly preferred elements may contain one of the novel developer-coupler compounds in one of the auxiliary layers.

The invention will be further illustrated but is not intended to be limited by the following procedures and examples.

Procedure A

N-(2'-hydroxy-5'-aminobenzyl)-3-hydroxyaniline

The preparation of this developer-coupler compound is typical of the production of the other developer-coupler compounds of the invention.

According to the procedure of Organic Synthesis Collective Vol. 3, pp. 468–469 (1955), p-nitrophenol is reacted with methylal and concentrated hydrochloric acid, in the presence of concentrated sulfuric acid, to yield 2-hydroxy-5-nitrobenzyl chloride. The product is then condensed with an aminophenol as follows:

In a 1-liter 2-necked flask, fitted with a reflux condenser and a dropping funnel, there were placed 0.2 mol of m-aminophenol and 400 ml. of ethanol. The mixture was heated to reflux until the solid dissolved, and then 0.1 mole of 2-hydroxy-5-nitrobenzyl chloride dissolved in 50 ml. ethanol was added through the dropping funnel over a period of 1 hour. Refluxing was continued for 4 hours. The ethanol was then distilled off (under reduced pressure during the final stages) and a residue obtained which was believed to be a mixture of N-(2'-hydroxy-5' -nitrobenzyl)-3-hydroxyaniline and 3-hydroxyaniline hydrochloride.

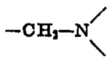
The residue was then dissolved in 0.8 mole of NaOH (10 percent solution in water) at room temperature and the nitro compound reduced by adding 0.3 mole of solid $Na_2S_2O_4$. After 15 minutes, the mixture was cooled by adding an equal volume of ice and neutralized with concentrated HCL (pH 6.5–7).

The precipitated, N-(2'-hydroxy-5'-aminobenzyl)-3-hydroxyaniline was filtered by suction and washed with 1 liter of a solution of Na_2SO_3 (50 g./liter). The precipitate was dried on a ceramic plate (not under vacuum). For preparing the sulfate, the dried compound was dissolved in 1 liter of ethanol and 10 ml. of 1 N. H_2SO_4 in ethanol was added. The black precipitate was removed by filtration, and the sulfate of the compound was precipitated by adding 90 ml. of 1 N. H_2SO_4 in ethanol.

The condensation reaction just described can be carried out with every reactant No. 1 with a molar ratio of 1:2 (e.g., 2-hydroxy-5-nitrobenzyl chloride:amine) or a molar ratio of 1:1:1 (e.g., 2-hydroxy-5-nitrobenzyl chloride:amine: sodium acetate). The second mole of amine or the sodium acetate acts as an HCl acceptor.

EXAMPLE 1

A TOTAL OF 38 developer-coupler compounds were prepared including the compound whose preparation was described in detail in procedure A. The organic synthesis of each of these compounds followed that described in procedure A by substituting appropriate reactants. In the table below, there are given the structural formulas of the 38 compounds along with the names and quantities of the reactants which are coupled through the



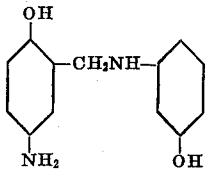
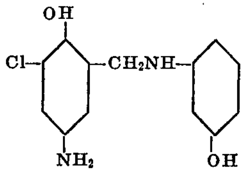
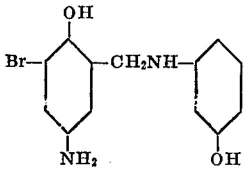
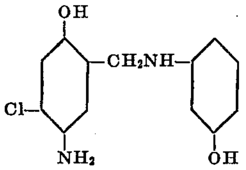
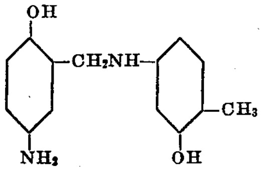
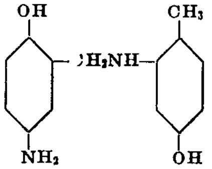
$$-CH_2-N\langle$$

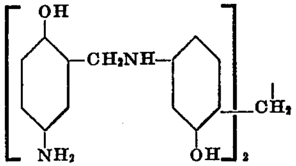
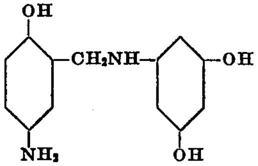
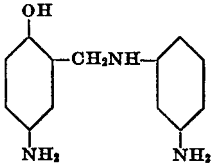
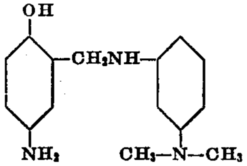
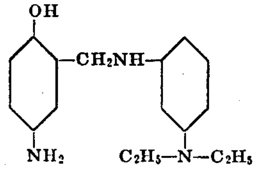
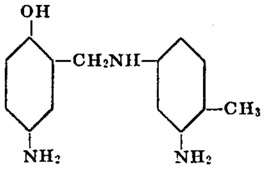
linkage, the quantity of hydrated sodium acetate (where employed) which was used in the condensation of reactants Nos. 1 and 2 to neutralize the acid which was formed as a by-product, the amounts of sodium hyposulfite and 10 percent sodium hydroxide used in reducing the nitro derivative to the final desired amino compound, the structural formulas of the developer-coupler compounds of this invention, and, in the last column, the color of the developed density. In this last column, for many of the compounds, there is given the color of the image with simple processing and another color (followed by a + sign) which resulted when development was followed by a treatment in an alkaline final bath. The final bath not only increases the image density but usually makes the image more black or blue-black in color.

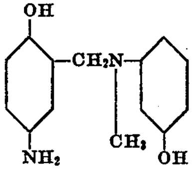
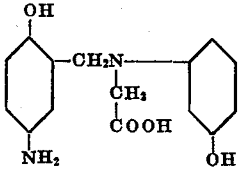
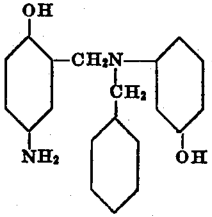
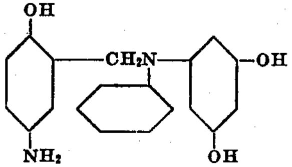
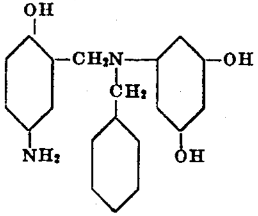
In the following table:

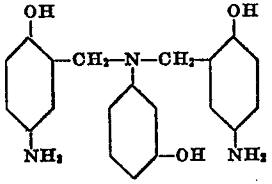
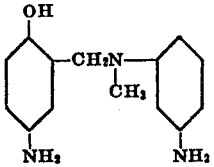
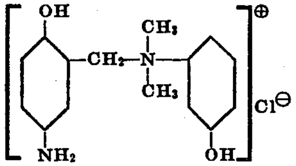
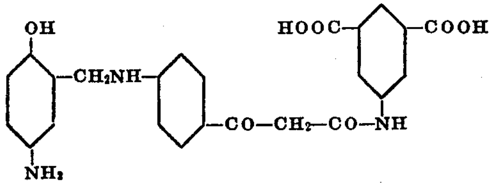
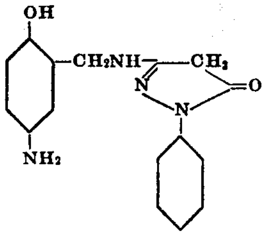
Compound A is 2-hydroxy-5-nitrobenzyl chloride
Compound B is 2-hydroxy-3-chloro-5-nitrobenzyl chloride
Compound C is 2-hydroxy-3-bromo-5-nitrobenzyl chloride
Compound D is 2-hydroxy-4-chloro-5-nitrobenzyl chloride

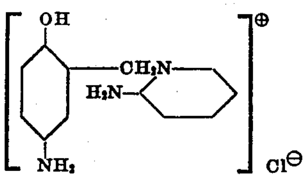
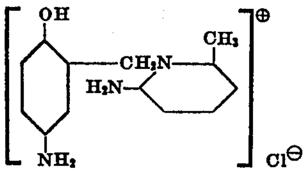
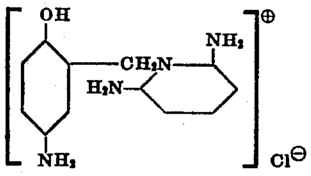
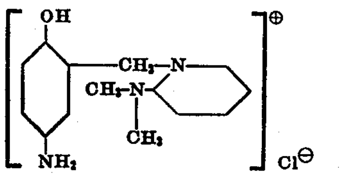
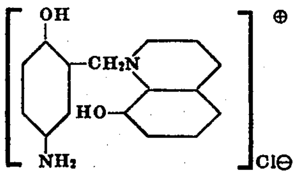
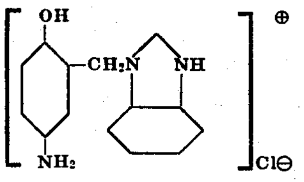
In the last column, the + sign means that a final alkaline bath was used.

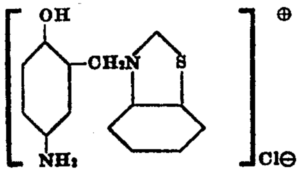
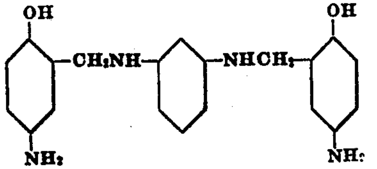
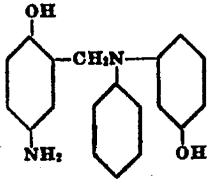
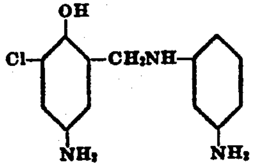
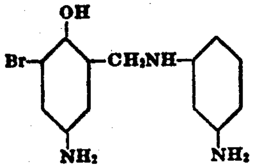
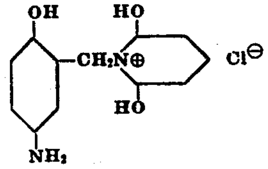
Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate ·3H_2O, grams	Reduction		Product	Developed color density
						NaOH, 10% ml.	$Na_2S_2O_4$, grams		
1	A	19	3-aminophenol	22		320	53		Brownish-black. Black+.
2	B	23	do	22		320	53		Brownish-black. Black+.
3	C	27	do	22		320	53		Brownish-black. Black+.
4	D	23	do	22		320	53		Brownish-black. Black+.
5	A	19	2-methyl-5-aminophenol	25		320	53		Brownish-black Black+.
6	A	19	3-amino-4-methylphenol	13	14	320	53		Brownish-black. Bluish-black+.

Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate $\cdot 3H_2O$, grams	Reduction		Product	Developed color density
						NaOH, 10% ml.	$Na_2S_2O_4$, grams		
7	A	38	2,2′-dihydroxy-4,4′-diaminodiphenylmethane	23	28	640	106		Brownish-black.
8	A	19	3,5-dihydroxyaniline	13	14	360	53		Do.
9	A	19	3-nitroaniline	28		520	106		Brownish-black. Black+.
10	A	19	N,N-dimethyl-3-aminoaniline	14	14	280	53		Brownish-black. Black+.
11	A	19	N,N-diethyl-3-aminoaniline	17	14	280	53		Brownish-black. Black+.
12	A	19	3-nitro-4-methylaniline	25		520	106		Brownish-black. Black+.

						Reduction			
Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate $\cdot 3H_2O$, grams	NaOH, 10% ml.	$Na_2S_2O_4$, grams	Product	Developed color density
13	A	19	N-methyl-3-aminophenol	13	14	320	53		Bluish-black.
14	A	19	3-aminophenol-N-acetic acid	17	14	360	53		Brownish-black.
15	A	19	N-benzyl-3-aminophenol.	19	14	320	53		Bluish-black.
16	A	19	N-phenyl-3, 5-dihydroxyaniline.	19	14	360	53		Brownish-black.
17	A	19	N-benzyl-3, 5-dihydroxyaniline.	21	14	360	53		Do.

Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate $\cdot 3H_2O$, grams	Reduction: NaOH, 10% ml.	Reduction: $Na_2S_2O_4$, grams	Product	Developed color density
18.	A	38	3-aminophenol	11		600	106		Do.
19.	A	19	N-methyl-3-nitroaniline	15	14	520	106		Bluish-black.
20.	A	19	N,N-dimethyl-3-aminophenol	14	14	320	53		Brownish-black. Bluish-black+.
21	A	19	4-amino-benzoyl-acet-3′,5′-dicarboxyanilide	68		360	53		Yellow.
22.	A	19	1-phenyl-3-aminopyrazolone-5	18	14	280	53		Orange. Magenta+.

Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate ·3H$_2$O, grams	Reduction NaOH, 10% ml.	Reduction Na$_2$S$_2$O$_4$, grams	Product	Developed color density
23	A	19	2-aminopyridine	10		280	53		Yellow.
24	A	19	2-amino-6-methylpyridine	11		280	53		Orange.
25	A	19	2,6-diaminopyridine	11		280	53		Magenta. Cyan +.
26	A	19	N,N-dimethyl-2-aminopyridine	13		280	53		Orange.
27	A	19	8-hydroxyquinoline	15		320	53		Magenta. Cyan+.
28	A	19	Benzimidazole	12		280	53		Orange.

Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate ·3H$_2$O, grams	Reduction: NaOH, 10% ml.	Reduction: Na$_2$S$_2$O$_4$, grams	Product	Developed color density
29	A	19	Benzthiazole	14		260	53		Do.
30	A	38	1,3-phenylenediamine	11	28	520	106		Brownish-black. Black+.
31	A	19	N-phenyl-3-hydroxyaniline	19	14	260	53		Bluish-black. Black+.
32	B	23	m-Nitroaniline	28		520	106		Brown. Black-violet.+
33	C	27	do	28		520	106		Brown. Black-violet+.
34	A	19	2,6-dihydroxypyridine	11		260	53		Blue.

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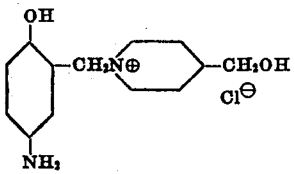
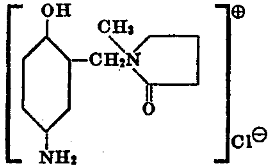
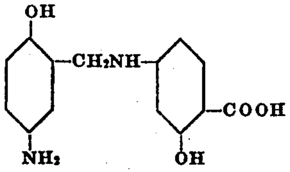
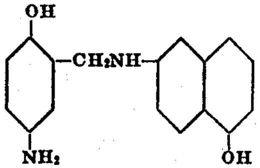
Product	Reactant No. 1 compound	No. of grams	Reactant No. 2	No. of grams	Sodium acetate ·3H₂O, grams	Reduction: NaOH, 10% ml.	Reduction: $Na_2S_2O_4$, grams	Product	Developed color density
35	A	19	4-hydroxymethylpyridine	11		320	53		Orange. Reddish-brown+.
36	A	19	N-methylpyrrolidone	10		280	53		Brown. Greenish-black+.
37	A	19	2-hydroxy-4-aminobenzoic acid	16	28	360	53		Brown. Bluish-black+.
38	A	19	2-amino-5-hydroxynaphthalene	16	28	320	53		Black.

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EXAMPLE II

Part A of an X-ray film having coated on each surface a gelatino-silver halide emulsion (AgBr:AgI = 60:1; gelatin: silver halide = 1:1; coating weight = 100 mg. $AgBr/dm.^2$) was exposed for 2 sec. to two Osram lamps (Wi 9 2660° K.) from a distance of 1.2 meters (20 lux at the wedge) to a gray-wedge with a wedge constant of D = 0.15/cm. with filters BG 3(1.8 mm.) + BG 38 (1.5 mm.) and developed for 3 minutes at 20° C, in a solution having the following composition:

N-(2′-hydroxy-5′-aminobenzyl) -3-hydroxyaniline [Compound 1 of Example 1]	5 g.
Na_2SO_3, anhydrous	50 g.
Potassium carbonate	75 g.
KBr	3 g.
Water to	1000 cc.

The film was then fixed for 2 minutes in 20 percent sodium thiosulfate solution, washed for 3 minutes, after-treated with a solution of 2 g. NaOH and 50 g. Na_2CO_3 in 1 liter water and dried.

Part B of the above described X-ray film was developed under the same conditions with a conventional developer solution having the following composition:

$K_2S_2O_5$	0.3 g.
1-Phenyl-3-pyrazolidone	0.3 g.
Disodium hexametaphosphate	2.0 g.
Ethylenediamine tetraacetic acid disodium salt	1.1 g.
Na_2SO_3, anhydrous	60.0 g.
Hydroquinone	15.0 g.
Na_2CO_3, anhydrous	50.0 g.
KNO_3	0.2 g.
Benztriazole	0.1 g.
KBr	3.0 g.
Water to	1000.0 cc.

The film was then fixed as described above, washed and dried without any alkaline after-treatment. The results obtained are as follows:

	Speed	Gradation	Fog	Dmax
Part A	74.9	2.0	0.12	3.6
Part B	74.0	1.8	0.09	1.5

EXAMPLE III

In the same procedure as described in example II N-(2′-hydroxy-5′-aminobenzyl)-3-hydroxyaniline was replaced by N-(2′-hydroxy-5′-aminobenzyl)-3-aminoaniline (compound 9 of example I).

The maximum densities thus obtained are as follows:

	Part A	Dmax =3.4
Control,	Part B	Dmax =1.5

EXAMPLE IV

In the same procedure as described in example II, the developer solution had the following composition:

N-(2′-hydroxy-5′-aminobenzyl) -3hydroxy-4-methylaniline (Compound 5 of Example I)	5 g.
Na_2SO_3, anhydrous	60 g.
Ascorbic acid	1 g.
KBr	2 g.
Na_2CO_3, anhydrous	50 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

	Part A	Dmax =3.5
Control.	Part B	Dmax =1.5

EXAMPLE V

Following the procedure of example IV, N-(2′-hydroxy-5′-aminobenzyl)-3-hydroxyaniline was replaced by N-bis(2′-hydroxy-5′-aminobenzyl)-3-hydroxyaniline (compound 18 of example I). The film was dried without any alkaline after treatment.

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.0
Control,	Part B	Dmax=1.5

EXAMPLE VI

In the procedure as described in example II, the films were developed for 1.5 minutes at 30° C.

	Part A	Dmax=3.5
Control,	Part B	Dmax=1.3

EXAMPLE VII

In the same procedure as described in example II the film was developed for 1 minute in a solution having the following composition:

N-methyl-N(2′-hydroxy-5′-aminobenzyl)-3-aminoaniline (Compound 19 of Example I)	8 g.
Na_2CO_3, anhydrous	100 g.
NaOH	10 g.
KBr	2 g.
Water to	1000 cc.

The film was dried without any alkaline after-treatment.

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.5
Control,	Part B	Dmax=1.5

EXAMPLE VIII

In the same procedure as described in example II the film was developed for 4 minutes in a solution having the following composition:

N(2′-hydroxy-5′-aminobenzyl) -2-methyl-5-hydroxyaniline (Compound 6 of Example I)	10 g.
Na_2CO_3, anhydrous	100 g.
Na_2SO_3, anhydrous	10 g.
KBr	0.5 g.
Water to	1000 cc

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.8
Control,	Part B	Dmax=1.5

EXAMPLE IX

In the same procedure as described in example II, the film was developed for 5 minutes in a solution having the following composition:

N(2′-hydroxy-3′-bromo-5′aminobenzyl)-3-hydroxyaniline (Compound 3 of Example I)	10 g.
Na_2CO_3, anhydrous	100 g.
KBr	1 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.3
Control,	Part B	Dmax=1.5

EXAMPLE X

In the same procedure as described in example II, the film was developed for 1.5 minutes in a solution having the following composition:

N(2'-hydroxy-5'-aminobenzyl)-3 (N,N-dimethylamino)-aniline (Compound 10 of Example I)	10 g.
Na_2CO_3, anhydrous	100 g.
NaOH	4 g.
KBr	20 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.4
Control,	Part B	Dmax=1.5

EXAMPLE XI

In the same procedure as described in example II the film was developed for 2 minutes in a solution having the following composition:

N(2'-hydroxy-5'-aminobenzyl)-N-phenyl-3,5-dihydroxyaniline (Compound 16 of Example I)	10 g.
Na_2CO_3, anhydrous	100 g.
NaOH	12 g.
N-methylpyrrolidone	5 g.
Water to	1000 cc.

The film was dried without alkaline after-treatment.

The maximum densities thus obtained are as follows:

	Part A	Dmax=2.5
Control,	Part B	Dmax=1.5

EXAMPLE XII

In the same procedure as described in example II the film was developed for 5 minutes in a solution having the following composition:

N,N'-bis(2''-dihydroxy-5''-aminobenzyl)-4,4'-diamino-2,2'-dihydroxy-diphenylmethane (Compound 7 of Example I)	5 g.
NaOH	4 g.
Na_2SO_3	50 g.
KBr	2 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

	Part A	Dmax=2.8
Control,	Part B	Dmax=1.5

EXAMPLE XIII

In the same procedure as described in example II, the film was developed for 2 minutes in a solution having the following composition:

N,N'-bis(2'-hydroxy-5'-amino benzyl)-1,3-phenylenediamine	5 g.

(The formula for this compound is that shown for compound 30 of example I.)

Na_2CO_3, anhydrous	100 g.
NaOH	4 g.
$NaSO_3$, anhydrous	50 g.
KBr	1 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

	Part A	Dmax=3.9
Control,	Part B	Dmax=1.5

EXAMPLE XIV

One side of an 0.007-inch film base was coated with an unsensitized fine-grain silver bromoiodide emulsion (gelatin: silver halide = 1; 5.5 mol % AgI). The coating weight was 100 mg. $AgNO_3$/ dm^2 and the emulsion thickness 0.0006 inch.

One part (A) of this material is provided with an overcoat made from the following solution:

30 g. Gelatin
12 ml. Aqueous solution of oleic acid methyl-tauride sodium salt, 8.3% by wt.
2 ml. Chrome alum (aqueous solution, 5% Cr by wt.)
H_2O to make 1 liter

The thickness of the overcoat is approximately 0.0001 inch.

A second (B) and third (C) part of the material were provided with an overcoat, which contains the sulfate of compound 1 of example I. These layers were coated from the following solution:

30 g. Gelatin
12 ml. Aqueous solution of oleic acid methyl-taruide sodium salt, 8.3% by wt.
20 g. Sulfate of N-(2'-hydroxy-5'-amino-benzyl)- 3-hydroxyaniline(=sulfate of Compound 1 of Example I)
2 ml. Chrome alum (aqueous solution, 5% Cr by wt.)
H_2O to make 1 liter

The thickness of this overcoat in each case was also approximately 0.0001 inch.

Part A, B and C were exposed behind a wedge in a sensitometer. Part A and B were then submitted to a conventional development in a developer containing

3 g.	N-methyl-p-aminophenol
60 g.	Na_2SO_3, anhydrous
3 g.	Hydroquinone
20 g.	Na_2CO_3, anhydrous
1 g.	KBr
H_2O	to make 1 liter

The thickness of this overcoat in each case was also approximately 0.0001 inch.

Part A, B and C were exposed behind a wedge in a sensitometer. Part A and B were then submitted to a conventional development in a developer containing

3 g.	N-methyl-p-aminophenol
60 g.	Na_2SO_3, anhydrous
3 g.	Hydroquinone
20 g.	Na_2CO_3, anhydrous
1 g.	KBr
H_2O	to make 1 liter

For use, one part of the developer is diluted with 2 parts of water. Developing time: 5 min. at 20° C.

Part A was then fixed for 5 min, in a fixing bath containing

250 g.	$Na_2S_2O_3 \cdot 5\ H_2O$
25 g.	$K_2S_2O_5$(Potassium pyrosulfite)
H_2O	to make 1 liter

washed for 5 min. and dried.

Part B was washed after development for 5 min., then fixed and washed as indicated above and finally treated for 3 min. in a solution of

1 g. NaOH/liter and 3 min. in a solution of

1 g. NaOH+5 g. Na_2CO_3 (anhydrous) per liter. Following this the sample was dried.

Part C was developed by immersing the sample for 5 min. at 20° C. in the following alkaline solution:

150 g.	Na_2CO_3, anhydrous
50 g.	Na_2SO_3 anhydrous
1 g.	KBr
H_2O	to make 1 liter

The film was then washed for 5 min., fixed and washed as indicated above and finally treated for 3 min. in a solution of

1 g. NaOH/liter and 3 min. in a solution of

1 g. NaOH+5 g. Na_2CO_3/liter. The sample is then dried.

The sensitometric results were as follows:

	Part A	Part B	Part C
Relative Speed	1.0	1.0	1.2
Gradation	0.9	1.7	1.33
Fog	0.05	0.13	0.14
Dmax	2.9	4.0	2.6

Example XV

Part A:

On one side of a 0.007-inch film base there was coated a layer from the following solution:

30 g.	Gelatin
12 ml.	Aqueous solution of oleic acid methyltauride sodium salt, 8.3% by wt.
40 g.	Sulfate of N-(2'-hydroxy-5'a minobenzyl)-3-hydroxyaniline (sulfate of Compound 1 Sulfate of Example I)
2 ml.	Chrome alum (aqueous solution, 5% Cr by wt.)
H_2O	to make 1 liter

When dry, on this layer there was coated a silver halide emulsion as in example VII (unsensitized fine-grain silver bromoidiode emulsion with a gelatin:silver halide ratio of 1 and 5.5 percent AgI). The emulsion was provided with an overcoat prepared from the following solution:

30 g.	Gelatin
12 ml.	Aqueous solution of oleic acid methyltauride sodium salt, 8.3% by wt.
2 ml.	Chrome alum (aqueous solution, 5% Cr by wt.)
H_2O	to make 1 liter

Part B:

On one side of a 0.0007-inch film base there was coated a layer from the following solution:

30 g.	Gelatin
12 ml.	Aqueous solution of oleic acid methyltaruride sodium salt, 8.3% by wt.
40 g.	Hydroquinone
2 ml.	Chrome alum (aqueous solution, 5% Cr by wt.)
H_2O	to make 1 liter

When dry, on this layer there was coated a silver halide emulsion and an overcoat as indicated for part A.

After being exposed in a sensitometer behind a wedge part A and B are developed by immersing for 5 min. at 20° C. into the following alkaline solution:

150 g.	Na_2CO_3, anhydrous
50 g.	Na_2SO_3, anhydrous
1 g.	KBr
H_2O	to make 1 liter

The samples are then washed for 5 min., fixed in an acid fixing solution, washed for 5 min. and finally treated for 3 min. in a solution of

1 g. NaOH/liter and 3 min. in a solution of

1 g. NaOH+5 g. Na_2CO_3 (anhydrous) per liter. The samples are then dried.

The sensitometric results were as follows:

	Part A	Part B	
Relative Speed	1.0		1.25
Gradation	1.24		0.75
Fog	0.02		0.02
Dmax	2.48		1.80
Coating Weight (mg. $AgNO_3/dm^2$)	52.0	74.0	

EXAMPLE XVI

An X-ray film coated on both sides with a gelatin-silver halide emulsion (AgBr:AgI = 60:1; gelatin:silver halide = 1:1; coating:150 mg. $AgBr/dm^2$) was developed for 6 minutes at 20° C. in a solution having the following composition:

[N'(2''-hydroxy-5''-aminobenzyl)-4'-aminobenzyl]-acetanilide 3,5-dicarboxylic acid (Compound 21 of Example I)	10 g.
Na_2CO_3, anhydrous	100 g.
KBr	1 g.
Water to	1000 cc.

The film was then fixed for 5 minutes in 20 percent sodium thiosulfate solution, washed for 5 minutes and dried.

Another part of the film was bleached after fixing in a solution of 50 g. $CuSO_4 \cdot 5H_2O$ and —50 g. NaCl in 1 liter of water for 5 minutes, then fixed, washed and dried as above.

The maximum densities thus obtained are as follows:

Dmax unbleached 2.0

Dmax bleached 0.5 (absorption max.: 380 μ at pH 7.)

EXAMPLE XVII

In the same procedure as described in example XVII the film was developed for 3 minutes in a solution having the following composition:

1-phenyl-3(2'-hydroxy-5'-aminobenzyl-amino)-pyrazolone-5 (Compound 22 of Example I)	10 g.
NaOH	0.4 g.
Na_2CO_3, anhydrous	100 g.
N-methyl-pyrrolidone	40 g.
KBr	1 g.
Water to	1000 cc.

The maximum densities thus obtained are as follows:

Dmax unbleached 2.9

Dmax bleached 2.0 absorption max.: 400, 520 μ at pH 7.

EXAMPLE XVIII

In the same procedure as described in example XVII the film was developed for 3 minutes in a solution having the following composition:

N(2'-hydroxy-5''-aminobenzyl)2,6-diamino-pyridinium chloride (Compound 25 of Example I)	10 g.
N-methyl-pyrrolidone	40 g.
NaOH	4 g.
KBr	2 g.
Water to	1000 cc

The maximum densities thus obtained are as follows:

Dmax unbleached	3.5
Dmax bleached	2.8(absorption max.:380, 670 mμ at pH 7.)

EXAMPLE XIX

To 200 ml. of an unsensitized fine-grain silver iodo-bromide emulsion (gelatin:silver halide × 1; 5.5 mole percent AgI) there were added 20 ml. of a solution containing 0.027 mole hydroquinone in methanol (part F).

To a second 200 ml. portion of the same emulsion there were added 20 ml. of an aqueous solution containing 0.018 mole (part G) of the sulfate of compound 1 of example I (sulfate of N-(2''-hydroxy-5''-aminobenzyl)-3-hydroxyaniline).

The emulsions were coated on one side of a 0.007-inch film base and each provided with an overcoat made from the following solution:

Gelatin	30 g.
Aqueous solution of oleic acid sodium salt, 8.3% by weight)	12 ml.
Chrome alum (5% Cr)	6 ml.
Water to	1 liter

When dry, the samples were exposed in a sensitometer under the following conditions:

Light source:	Osram Wi 43, color temperature 2,260° K.
Distance of light source to wedge.	120 cm.
Brightness at the wedge:	36 lux
Wedge:	continuous wedge constant:D=0.15 cm.
Exposure time:	4.5 sec.

The speed was measured at D=0.3 above fog.

The gradation is defined as the slope of the straight line connecting the points on the density curve corresponding to D=0.3 and D=1.6 above fog.

The samples were then developed for 5 min. at 20° C. in an alkaline solution containing:

Na_2CO_3, anhydrous	150 g.
Na_2SO_3, anhydrous	50 g.
KBr	1 g.
Water to	1 liter

Part F was then fixed for 5 min. in a fixing bath, containing

$Na_2S_2O_3 \cdot H_2O$	250 g.
$K_2S_2O_5$ (Potassium pyrosulfite)	25 g.
Water to	1 liter

The film was then washed for 5 minutes and then dried. part G was washed after development for 5 minutes in tap water, fixed and washed as indicated for part F and finally immersed for 3 minutes in a solution of:

NaOH +	0.4 g.
Ascorbic acid	0.15 g. per liter

and for 3 minutes in a solution of:

NaOH	0.4 g.
Na_2CO_3	5.0 g.
Ascorbic acid	0.15 g. per liter

The samples were then dried.

The results were as follows:

	Part F	Part G
Silver coating weight ($AgNO_3$/ dm.^{2})	73.2 mg.	67.2 mg.
Developing agent	Hydroquinone	Sulfate of compound 1
(moles per Kg. emulsion)	0.135	0.09
Relative speed	1.0	1.1
D_{max}	2.8	4.5
Fog	0.06	0.08
Graduation	1.08	2.25

EXAMPLE XX

Part A of an X-ray film having coated on each surface a gelatino-silver halide emulsion (AgBr:AgI=60:1; gelatin: silver halide = 1:1; coating weight = 100 mg. AgBr/dm.^{2}) was exposed for 2 sec. to two Osram lamps (Wi 9,2660° K.) from a distance of 1.2 meters (20 lux at the wedge) to a gray-wedge with a wedge constant of D=0.15/cm. with filters BG 3 (1.8 mm.) + BG 38 (1.5 mm.) and developed for 3 minutes at 20° C. in a solution having the following composition:

N-(2′-hydroxy-5″-aminobenzyl)-3-hydroxy aniline (compound 1 of the table)	5 g.
N-methyl-N(2″-hydroxy-5″-aminobenzyl) 3-amino-aniline (compound 19 of the table)	5 g.
Na_2SO_3, anhydrous	50 g.
Na_2CO_3, anhydrous	25 g.
NaOH	2 g.
$NaBO_2 \cdot H_2O$	70 g.
KBr	10 g.
Water to	1,000 cc.

The film was then fixed for 2 minutes in 20 percent sodium thiosulfate solution, washed for 3 minutes and dried.

Part B of the above-described X-ray film was developed under the same conditions with a conventional developer solution having the following composition:

$K_2S_2O_5$	0.3 g.
1-phenyl-3-pyrazolidone	0.3 g.
Disodium hexametaphosphate	2.0 g.
Ethylenediamine tetraacetic acid disodium salt	1.1 g.
Na_2SO_3, anhydrous	60.0 g.
Hydroquinone	15.0 g.
Na_2CO_3, anhydrous	50.0 g.
KNO_3	0.2 g.
Benztriazole	0.1 g.
KBr	3.0 g.
Water to	1,000.0 cc.

The film was then fixed as described above, washed and dried. The maximum densities thus obtained are as follows:

Part A	Dmax=4.1
Control, Part B	Dmax=1.5

EXAMPLE XXI

In the same procedure as described in example XX, the film was developed for 3 minutes in a solution having the following composition:

N-methyl-N(2′-hydroxy-5′-aminobenzyl)-3-hydroxy aniline (compound 13 of the table)	5 g.
N-(2′-hydroxy-5″-aminobenzyl)-3-amino aniline (compound 9 of the table)	5 g.
Na_2SO_3, anhydrous	50 g.
$NaBO_2 \cdot H_2O$	140 g.
KBr	2 g.

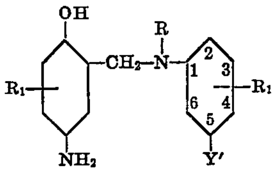
The maximum densities thus obtained are as follows:

Part A	Dmax=3.2
Control, Part B	Dmax=1.5

An important advantage of the invention lies in the ability to develop photographic films of low silver halide content to high densities. The constantly rising price of silver is, of course, a matter of great concern in the photographic industry. For example, an X-ray film containing 100 mg. $AgNO_3$/dm.^{2} has a density of about 1.5 when developed by the customary methods, while on using the developer substances of the invention a density of 3.0 can be obtained. In order to achieve such a density with conventional developers, about 200 mg. $AgNO_3$/dm.^{2} would be required. With a constant ratio of gelatin to silver the savings in silver halide would also be a saving in gelatin. The two savings together lead to a diminution in film thickness with the accompanying advantages, such as rates of processing and drying. Improvements have also been found in the gradient or contrast of the developed image as well as in the apparent speed or light sensitivity of the emulsion developed in the presence of the novel developer-coupler compounds of this invention. A number of developer/coupler compounds are capable of forming color images. Thus, by proper choice of compounds it becomes possible to prepare an element capable of recording full color images.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. The compound of the formula:



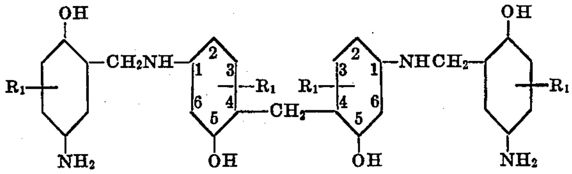
wherein the rings are benzene rings,

R is H, alkyl of one to four carbon atoms, benzyl, carboxymethyl or phenyl,

R_1 is H, alkyl of one to four carbons, Cl, Br, or COOH, and Y' is –OH or –NH_2

and at least one of the coupling positions 2 and 4 is a free coupling position.

2. The compound of the formula:



wherein

R_1 is H, alkyl of one to four carbons, C1, Br or COOH, and at least one of the positions 2– is a free coupling position.

3. N-(2-hydroxy-5-aminobenzyl)-3-hydroxyaniline.

4. N-(2-hydroxy-5-aminobenzyl)-3-hydroxy-4-methylaniline.

5. N-(2-hydroxy-5-aminobenzyl)-2-methyl-5-hydroxyaniline.

6. N-(2-hydroxy-5-methylaminobenzyl)-3-aminoaniline.

7. N,N'-bis(2-hydroxy-5-aminobenzyl)-1,3-phenylenediamine.

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