United States Patent [19]

Bard

[11] **3,818,078**

[45] **June 18, 1974**

[54] **PHOTOGRAPHIC SILVER HALIDE DEVELOPING AGENTS**

[75] Inventor: **Charleton C. Bard,** Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

[22] Filed: **July 6, 1971**

[21] Appl. No.: **160,179**

Related U.S. Application Data

[60] Division of Ser. No. 801,138, Feb. 20, 1969, Pat. No. 3,592,652, which is a continuation-in-part of Ser. No. 639,274, May 18, 1967, abandoned.

[52] **U.S. Cl.**..... **260/509,** 260/465 D, 260/465 E, 260/517, 260/519, 260/556 A, 260/556 AR

[58] **Field of Search**..... 260/556 A, 556 AR, 509, 260/465 D, 465 E, 517, 519

[56] **References Cited**

UNITED STATES PATENTS

3,592,652 7/1971 Bard 96/55

Primary Examiner—Henry R. Jiles
Assistant Examiner—C. M. S. Jaisle
Attorney, Agent, or Firm—Alfred P. Lorenzo

[57] **ABSTRACT**

Monocyclic and bicyclic phenols containing at least one sulfonamido group, especially an aromatic sulfonamido group, and a nitrogen containing radical (which may be a sulfonamido group), are described. They are photographic silver halide developing agents for black-and-white development, but are especially useful as competing or balancing developing agents in photographic color developers to control amount of dye produced by the color developer, especially those containing the color-former or coupler.

6 Claims, No Drawings

PHOTOGRAPHIC SILVER HALIDE DEVELOPING AGENTS

This application is a division of my U.S. Pat. application Ser. No. 801,138 filed Feb. 20, 1969 and issued July 13, 1971 as U.S. Pat. No. 3,592,652 which was in turn a continuation-in-part of my U.S. Pat. application Ser. No. 639,274 filed May 18, 1967, now abandoned.

This invention relates to photographic silver halide developing agents and photographic developers containing them. Such developing agents can be used in "negative" or black-and white developers, but are especially useful in photographic developers adapted for use in color development to produce a colored image record.

BACKGROUND

In the color development of multicolor photographic elements it is known that competing or "balancing" developing agents can be used to regulate the amount of dye formed, and thereby control the overall color reproduction characteristics of the color photographic material. Two types of competing, or so-called balancing developing agents, have been used in color processes, usually reversal color processes wherein the color formers or couplers are in the color developer solution, i.e.:

1. An upper-scale, contrast-modifying and maximum density adjustor which is normally a black-and-white developing agent; examples of this type of balancing developing agent are p-methylaminophenol, 1-phenyl-3-pyrazolidone, hydroquinones, and 2,4-di-aminophenol;
2. A "toe-chopping" developing agent in which the dye maximum density does not change, but the amount of the dye in the minimum density or "toe" portion of the plot of density against Log. exposure (H and D curve) is reduced. An outstanding example of this type of balancing developing agent is N-benzyl-p-aminophenol (MBAP). This invention is primarily concerned with the latter type of color control.

PRIOR ART

Many of the known competing developing agents have the disadvantage that their oxidation and hydrolysis by-products cause imagewise formation of a substantive green-light-absorbing impurity which degrades the color quality of greens and cyans by increasing the green absorption of the cyan dye image. One by-product, p-aminophenol, formed from MBAP causes this problem. Benzaldehyde, a product formed from MBAP, reacts with unused p-phenylenediamine color developer to form an oily Schiff's base that tends to produce a tacky dirt in the developer which sticks to the film being processed. Attempts to control the dirt, formed as a result of the oxidation of MBAP, and the hue shift produced by the undesirable coupling of p-aminophenol, have made it necessary to add additional chemicals to the color developer solutions which not only increase the cost of the required materials but also increase the problem of chemical control or balance. Because of this there has been a long sustained search for a better "toe-chopping" developing agent which will give the desired sensitometric control without producing oxidation products that form "dirt" and/or color absorbing materials that degrade color quality.

OBJECTS

It is therefore an object of my invention to provide competing developing agents which are valuable "toe-chopping" developing agents and do not lower the D-max. of the developed image dyes when used at low concentrations in developers, and which at higher concentrations are also useful as upper-scale, contrast-reducing developing agents without forming green-absorbing impurities which degrade the color quality of greens and cyans.

Another object of my invention is to provide competing developing agents whose oxidation products not only do not produce unwanted dye, but also do not produce tacky dirt which is characteristic of certain competing developing agents that are presently used on a large scale.

Another object is to provide new silver halide developing agents for black-and-white and color photography.

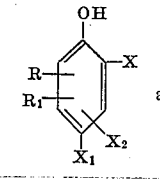
Still further objects will become apparent from the following specification and claims.

BRIEF DESCRIPTION OF INVENTION

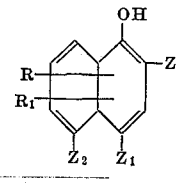
These and other objects are accomplished according to my invention by providing phenolic silver halide developing agents containing a monocyclic or bicyclic phenolic group having at least one sulfonamido substituent. When the phenolic compound has a monocyclic phenolic group or radical, the carbon atoms in the 2- and 4-positions of the monocyclic ring are each connected to a nitrogen atom and one of the nitrogen atoms is the nitrogen atom of a sulfonamido group and the other nitrogen atom is the nitrogen atom of a sulfonamido group or the nitrogen atom of an amino group, and when the phenolic developing agent has a bicyclic phenolic group or radical structure, at least one (usually two) of the carbon atoms in the 2, 4 or 5 positions of the bicyclic ring structure is connected to the nitrogen atom of a sulfonamido group, and the bicyclic phenolic group contains at least one additional N-substituent, usually a sulfonamido substituent.

MORE DETAILED DESCRIPTION

The phenolic silver halide developing agents of my invention include those represented by the following general formulas:

I. 

and

II. 

wherein X and X_1 each represents a

A. 

group or a

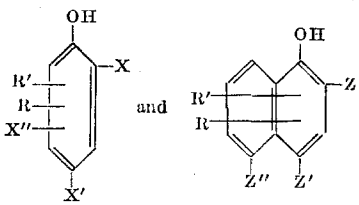
B. 

group, at least one of X and X_1 being a B group as depicted above; X_2 represents hydrogen an amino group (including amino groups of the class defined by A above) or a sulfonamido group (including a B group as defined above); R and R_1 each represents hydrogen, an alkyl group, substituted or unsubstituted (including, for example, methyl, ethyl, propyl, beta-sulfoethyl, gamma-sulfobutyl, carboxymethyl, gamma-carboxypropyl, beta-hydroxyethyl, gamma-hydroxypropyl, gamma-hydroxybutyl, including alkali metal and ammonium salt forms of the alkyl groups containing a sulfo or carboxyl radical), an alkoxyl group (e.g., methoxyl, ethoxyl, propoxyl, etc.), an acyl group (e.g., acetyl, butyryl, benzoyl, p-toluoyl, etc.), halogen (e.g., chlorine, bromide, fluorine, etc.), or cyano; R_2, R_3 and R_4 each represents hydrogen, an alkyl group, substituted or unsubstituted (including, for example, such alkyl groups as defined above for R and R_1) or an aryl group (e.g., phenyl, p-carboxy, p-sulfophenyl, o-ethoxyphenyl, o-chlorophenyl, p-nitrophenyl, etc.); Q represents an alkyl group, especially such groups containing from 1–8 carbon atoms (e.g., methyl, ethyl, butyl, beta-sulfoethyl, gamma-sulfobutyl, carboxymethyl, gamma-carboxypropyl, beta-hydroxyethyl, benzyl (phenylmethyl), phenethyl, n-octyl, etc.) or an aryl group (e.g., phenyl, p-carboxyphenyl, p-sulfophenyl, p-ethoxyphenyl, p-tolyl, o-chlorophenyl, p-nitrophenyl, alpha-naphthyl, beta-naphthyl, p-carboxynaphthyl, p-sulfonaphthyl, etc., including alkali metal and ammonium salts of said radicals containing a sulfo or carboxy radical) and Z, Z_1 and Z_2 each represents hydrogen, an amino group (including such groups as those defined by the A group above) or a sulfonamido group (including such groups as defined by the B group above), at least one of Z, Z_1 and Z_2 being a sulfonamido group, such as the B group above, and at least one of Z, Z_1 and Z_2 being a nitrogen containing substituent wherein the N-atom is directly attached to the bicyclic phenolic ring. At least one Q group is usually aryl.

Included among typical compounds represented by formulas I and II are the following:

1. 5-Benzenesulfonamido-2-methanesulfonamido-1-naphthol
2. 2,4-Bis(benzenesulfonamido)phenol
3. 4-Benzenesulfonamido-2-(p-toluenesulfonamido) phenol
4. 2,4-Bis(p-toluenesulfonamido)phenol
5. 2,4-Bis(benzenesulfonamido)-5-methylphenol
6. 2-Amino-4-benzenesulfonamidophenol
7. 2,4-Bis(N-methyl-benzenesulfonamido)-5-sulfophenol
8. 2,5-Bis(benzenesulfonamido)-1-naphthol
9. 2,4,5-Tris(benzenesulfonamido)-1-naphthol
10. 2,4-Bis(methanesulfonamido)-5-methylphenol
11. 2-Methanesulfonamido-4-benzenesulfonamidophenol

In a more particular aspect, the silver halide developing agents of my invention are selected from compounds having one of the formulas:



wherein X represents a $-N\overset{L}{<}SO_2Q$ group; X′ represents a $-N\overset{L'}{<}SO_2Q'$ group; X″ represents a member of the class consisting of hydrogen and a $-N\overset{L}{<}SO_2Q$ group; L and L′ each represents a member of the class consisting of hydrogen, methyl, ethyl, propyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, hydroxypropyl, hydroxybutyl; Q and Q′ each represents a member of the class consisting of methyl, ethyl, butyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, benzyl, phenethyl, octyl, phenyl, 4-carboxyphenyl, 4-sulfophenyl, 2-ethoxyphenyl, 4-methylphenyl, 2-chlorophenyl, 4-nitrophenyl, α-naphthyl, β-naphthyl, 4-carboxynaphthyl, 4-sulfonaphthyl; R and R′ each represents a member of the class consisting of hydrogen, methyl, ethyl, propyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, methoxy, ethoxy, propoxy, acetyl, butyryl, benzoyl, 4-methylbenzoyl, halogen and cyano; Z represents a member of the class consisting of hydrogen and a $-N\overset{L}{<}SO_2Q$ group; Z′ represents a member of the class consisting of hydrogen and a $-N\overset{L}{<}SO_2Q'$ group; Z″ represents a member of the class consisting of hydrogen and a $-N\overset{L}{<}SO_2Q$ group; with the proviso that at least two of Z, Z′ and Z″ are not hydrogen.

In their simplest form, my developing compositions comprise (1) one of my phenolic silver halide developing agents and (2) a second silver halide developing agent.

Typical examples of such second silver halide developing agents used in my novel developer compositions are the following:

a. non-color forming silver halide developing agents, i.e., developing agents whose oxidation products do not couple with color-forming couplers including developing agents, such as, a hydroquinone (e.g., hydroquinone, methylhydroquinone, chlorohydroquinone, etc.), a 1-phenyl-3-pyrazolidone (e.g., 1-phenyl-3-pyrazolidone, 4-methyl-1-phenyl-3-pyrazolidone, 4,4-dimethyl-1-phenyl-3-pyrazolidone, etc.), p-methylaminophenol, 2,4-diaminophenol, ascorbic acid, etc.; and

b. color-forming silver halide developing agents, i.e., developing agents whose oxidation products couple with color-forming couplers to form colored images, including the primary aromatic amino color developing agents (e.g., p-phenylenediamine, the alkyl phenylenediamines, the alkyl toluenediamines, etc., which have one primary amino group).

Developing compositions comprising my phenolic silver halide developing agents and such second non-color forming silver halide developing agent (a) above are advantageously used to make developer solutions that show synergistic effects in black-and-white photography. For example, combinations of 2,4-bis(benzenesulfonamido)phenol with hydroquinone produce a synergistic effect that is illustrated later herein.

The developing compositions of my invention can also contain any of the various components that are normally in photographic developing solutions and include materials such as alkalies, alkali metal sulfites, alkali metal bisulfites, alkali metal thiocyanates, alkali metal bromides, alkali metal iodides, thickening agents

(e.g., carboxymethyl cellulose, etc.), water softening agents, etc.

Color-forming couplers are used to advantage in color developer for compositions used to prepare a color developer for a color film that does not contain incorporated color-forming couplers. Particularly efficacious compositions for making color developing solutions comprise one of my competing developing agents, a primary aromatic amine color developing agent and a hydroxylamine, e.g., hydroxylaminesulfate, N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine. I have found that a marked synergism results by combining my competing developing agent and a hydroxylamine which makes it possible to use much lower concentrations of my competing developing agent than would otherwise be needed.

Any of the well-known alkali-soluble coupler compounds can be used to advantage in my color developer solutions. See U.S. Pat. No. 3,300,305, issued Jan. 24, 1967 for a summary of such couplers. Useful cyan dye-forming couplers include the alkali-soluble diffusible couplers such as the naphthols, nitronaphthols, hydroxynaphthoic acetamides, acylaminophenols, diacylaminophenols, and others,

Magenta dye-forming couplers which are useful in my color developer solutions include the alkali-soluble diffusible couplers such as the pyrazolones, sulfonamide substituted pyrazolones, acylated aminopyrazolones, halogen substituted pyrazolones, coumarones, etc.

Yellow dye-forming couplers which are useful in my color developers include the alkali-soluble diffusible couplers such as the acylacetanilides, sulfonamide-substituted acylacetanilides, etc.

My compounds are used to advantage in compositions over a wide range of concentrations. Usually, for purposes of "toe-chopping," concentrations in the range from about 0.1 g/l to about 10 g/l are used to advantage with a preferred concentration being in the range from about 0.1 to about 2 grams per liter. I have found a marked synergism between hydroxylamine and my novel competing developing agents which further extends the useful concentration range over which my competing developers may be used. For example, only from about 0.1 to about 0.2 gram per liter of my competing developing agent is needed in the presence of about 5 grams per liter of hydroxylamine sulfate in order to obtain the desired "toe-chopping" effects. At a concentration of about 0.5 gram per liter of my competing developing agent about 0.25 gram per liter of hydroxylamine sulfate is used to advantage, while at concentrations of about 1 gram per liter of my competing developing agent, no hydroxylamine sulfate is needed. Usually when reduction in the contrast in the shoulder or D-max. portion of the sensitometric curve is desired, higher concentrations of my competing developing agents are used to advantage usually in the range from about 2 grams per liter to about 20 grams per liter. The optimum concentration can be determined by methods well known in the art, that is, by making studies of the results given by systematic variations in concentration of these components.

During use, my competing developing agents do not couple with oxidized color developing agents in the developer solutions to form dyes as do many of the prior art competing developing agents. Another advantage which is provided by use of my competing developing agents is that they do not oxidize to form compounds which produce tacky dirt in the color developer solutions.

Use of my balancing developing agents has made it possible to replace the MBAP, and the hydroxylamine (wholly or partly) that are used in certain commercially used color developing solutions. In certain instances, though, as mentioned before, it may be desired to use hydroxylamine in order to obtain the synergistic effect with my balancing developing agents.

My competing developing agents are used to advantage in compositions used for making color developer solutions containing any of the well-known primary amino silver halide developing agents, such as the p-phenylenediamines including the alkyl phenylenediamines and alkyl toluenediamines. These developing agents are usually used in salt form, such as the hydrochloride or sulfate, which are more stable than the free amine. The p-aminophenols and their substitution products can also be used as color developing agents when the amine group is unsubstituted. Typical examples of p-phenylenediamine developers include substituted p-phenylenediamines, such as the N-alkylsulfonamidoalkyl-p-phenylenediamines, the sulfonamido substituted p-phenylenediamines, etc. All of these color developing agents have an unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming products to form a dye image. Included among the color developers are, such typical illustrative examples as, 2-amino-5-diethylaminotoluene hydrochloride, N-ethyl-beta-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate, 4-amino-N,N-diethyl-3-methylaniline hydrochloride, 4-amino-N-ethyl-N-(beta-methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate, 3-methyl-p-aminodiethylaniline sulfate, 4-amino-N-ethyl-N-(beta-hydroxyethyl)aniline sulfate, N,N-dimethyl-p-phenylenediamine hydrochloride, etc.

In general, the phenolic silver halide developing agents of my invention having sulfonamido substituent(s) are advantageously prepared by reacting the corresponding amino substituted phenolic compound dissolved in a suitable inert organic solvent, such as pyridine, with the appropriately substituted sulfonyl chloride having the formula:

$$QSO_2Cl$$

wherein Q is as defined previously. The crude product is precipitated from the reaction mixture by pouring over ice and hydrochloric acid, separated by filtration and purified by recrystallization from appropriate organic solvents.

My silver halide developing agents which have 2 (or 3) different sulfonamido substituents are advantageously prepared by reacting the appropriate phenolic intermediate having one amino group and one (or two) nitro groups with the appropriately substituted sulfonyl chloride. The intermediate formed is isolated as described, then the nitro group(s) on the intermediate is reduced to the amino group(s) by well-known catalytic hydrogenation reactions (e.g., with hydrogen and Raney nickel), followed by reaction with the appropriate substituted sulfonyl chloride. The final crude product is isolated and purified using the techniques described above.

The following specific syntheses will still further illustrate my invention.

EXAMPLE A

Into a four-neck, 1 liter flask, equipped with mechanical stirrer, condenser, thermometer and well, solid addition port and nitrogen bleed were placed 18.4 g. (0.1 mol.) of 2,4-dinitrophenol, 175 cc. of methanol and 200 cc. (2.3 mol.) of hydrochloric acid. The mixture was steam-heated to a pot temperature of 50°C. and 40 g. (0.715 mol.) of plast iron were added in small amounts of 70°–80°C. at which time steam was shut off and iron addition was continued at a rate to maintain a pot temperature between 70°–80°C. until the entire 5 g. of iron had been added. The addition was performed under a hood because the odor of hydrogen sulfide was present. Upon completion of the iron addition, steam was applied to maintain a reflux for 30 minutes. The dark green heterogeneous mixture was then water-cooled to 10°–15°C. and the crude dihydrochloride of 2,4-diaminophenol was collected in a funnel and washed with 50 cc. of cold acetic acid. The grayish product was immediately transferred to a suitable flask containing 100 cc. of water previously purged with nitrogen in order to prevent air-oxidation and excessive color. To this flask were added 10 cc. of acetic acid and 2 g. of Pitt. carbon. The mixture was heated to 50°–70°C. for 5 minutes, filtered through a Super-Cel pad and the light tan solution was immediately transferred to a suitable vessel purged with nitrogen.

The pot temperature was adjusted to 20°–30°C. and 36 g. (0.204 mol.) of benzenesulfonyl chloride and 35 g. (0.426 mol.) of sodium acetate were added. To the mixture 80 cc. of acetic acid were added and the mixture was heated with stirring to a pot temperature of 70°–80°C. for 1½ hours. On cooling some product began to separate at 50°C. Water (100 cc.) were added and the mixture was cooled to 10°–15°C., and 2,4-bis(-benzene-sulfonamido) phenol were collected by filtration and washed with two 50 cc. portions of 50°C. water. The pale lavender solid had a melting point of 193°C. and was obtained in a yield of 87 percent (35 g.). The resulting product was further purified by dissolving it in 100 cc. of methanol, filtering and adding to 300 cc. of water containing 2 g. of sodium dithionite. An odor of sulfur dioxide was present, but the product when collected and washed with water was white and had a melting point of 193°C. The dried purified product weighed 32 g.

EXAMPLE B

4-Benzenesulfonamido-2-(p-toluenesulfonamido)phenol, Compound 3, was advantageously prepared by reacting one molar equivalent of 2-amino-4-nitrophenol in pyridine with one molar equivalent of p-toluenesulfonyl chloride. The crude product, 2-(p-toluenesulfonamido)-4-nitrophenol was isolated, purified, and then reduced to 4-amino-2-(p-toluenesulfonamido)phenol by catalytic hydrogenation. The amino-intermediate was dissolved in pyridine and reacted with an equimolar amount of benzenesulfonyl chloride. Compound 3 was isolated and purified by methods similar to those described in Example A.

Compound 4 is advantageously prepared like Compound 2 but using 2 molar equivalents of p-toluenesulfonyl chloride in place of benzenesulfonyl chloride.

Compound 5 is prepared like Compound 2 but using an equimolar amount of 2,4-diamino-5-methylphenol in place of 2,4-diaminophenol.

EXAMPLE C

Compound 6 was advantageously prepared by reacting one mole of 4-amino-2-nitrophenol dissolved in pyridine with one mole of benzenesulfonyl chloride dissolved in pyridine. The crude 4-benzenesulfonamido-2-nitrophenol formed was separated by pouring the reaction mixture over cracked ice and concentrated HCl acid. After the crude product crystallized, it was separated by filtration, dissolved in alkaline solution, treated with activated carbon, filtered and HCl acid added to make the filtrate acidic to Congo Red paper. The precipitated 4-benzenesulfonamido-2-nitrophenol was then separated by filtration and purified by recrystallization from a suitable solvent such as benzene. To an aqueous alkaline solution of the purified 4-benzenesulfonamido-2-nitrophenol was added in small portions sodium dithionite until the original deep reddish color was discharged while enough sodium hydroxide was added to prevent precipitation. When the reaction was complete, the product (Compound 6) was precipitated by neutralizing the solution with HCl acid. The crude compound 6 was washed with cold 1 percent sodium bisulfite solution and then recrystallized from 0.1 percent sodium bisulfite containing a few percent of ethanol. The purified compound 6 had a melting point of 170°–171°C.

Compound 7 is advantageously prepared like Compound 2 by reacting one mole of 2,4-bis(methylamino)-5-sulfophenol with two moles of benzenesulfonyl chloride dissolved in pyridine. After completion of the reaction, the reaction mixture is poured over ice and HCl acid, and the product separated and purified by methods similar to those described previously.

Compound 8 is advantageously prepared by a method similar to that used for Compound 2 but by reacting one mole of 2,5-diamino-1-naphthol with two moles of benzenesulfonyl chloride.

Compound 9 is advantageously prepared by a method similar to that used to prepare Compound 2 but using three molar equivalents of benzenesulfonyl chloride with one molar equivalent of 2,4,5-triamino-1-naphthol.

Compound 10 is advantageously prepared by a method similar to that used to make Compound 2 but in which one mole of 2,4-diamino-5-methylphenol is used in place of 2,4-diaminophenol and in which methanesulfonyl chloride is used in place of benzenesulfonyl chloride.

Compound 11 is advantageously prepared by a method similar to that used to make Compound 3 but reacting one molar equivalent of 2-amino-4-nitrophenol in pyridine with one molar equivalent of methanesulfonyl chloride, isolation of the 2-methanesulfonamido-4-nitrophenol formed, catalytic hydrogenation of this compound to 2-methanesulfonamido-4-aminophenol followed by reaction of this amino compound with an equimolar amount of benzenesulfonyl chloride. The crude product Compound 11 is isolated and purified by methods similar to those described previously.

Compounds 4 to 11 can be similarly prepared and purified as described in Examples A and B.

The following examples will illustrate the preparation and use of photographic developers useful in my invention.

EXAMPLE 1

A dry composition was made containing 8 grams of hydroquinone and 8 grams of 2,4-bis(benzenesulfonamido)phenol (Compound 2). This composition was used to make one liter of a developer solution having the composition:

Developer A

Hydroquinone	8	g.
2,4-Bis(benzenesulfonamido)phenol	8	g.
Sodium sulfite, desiccated	90	g.
Sodium carbonate monohydrate	52.2	g.
Potassium bromide	5	g.
Water to make	1	liter

For comparison Developers B and C (both outside my invention) were made. Developer B was similar to Developer A but the 2,4-bis(benzenesulfonamido)phenol was omitted. Developer C was similar to Developer A but the hydroquinone was omitted. Three pieces of a conventional camera-speed reversal film containing a gelatino silver bromoiodide emulsion were each given an exposure of 2.3×10^{-2} meter candle seconds to a 6,100°K. light source. Each of the three pieces of exposed film, identified as strips 1, 2 and 3, was developed at 70°F. for 5 minutes in one of Developers A, B and C respectively, immersed 30 seconds in an acid stop bath, then immersed 5 minutes in a conventional alkali metal thiosulfate fix bath, and finally given a 10 minute water-wash and dried. This procedure was repeated using three more pieces of the same unexposed film, but giving each piece an exposure of 9.3×10^{-2} meter candle seconds to a light source of 6,100°K. The exposed strips identified as Strips 4, 5 and 6 were given the same processes as strips 1, 2 and 3, respectively. The amount of developed silver per unit area in each of strips 1 through 6 was determined by well known X-ray fluorescence techniques. The results are summarized in Table 1.

Table 1

Strip	Exposure Meter Candle Seconds 6100°K	Concentration in g/l of Developing Agents in Developer Solution: Hydroquinone	Developing Agent No. 2	Theoretical Sum of Silver Developed By Each Developing Agent in μg/cm²	Actual Silver Developed in μg/cm²
3	2.3×10^{-2}	8	0	0	0
2	do.	0	8	0	0
1	do.	8	8	0	10
6	9.3×10^{-2}	8	0	—	2.5
5	do.	0	8	—	12.5
4	do.	8	8	15	60.0

The results show that a combination of hydroquinone and 2,4-bis(benezenesulfonamido)phenol (Developing Agent No. 2) in a conventional developer solution produces 4 times the amount of silver in the film given 9.3 $\times 10^{-2}$ meter candles second exposure that would be expected, based on the amounts of silver developed by a similar developer from which one or the other of the two developing agents was omitted. In the film strips given 2.3×10^{-2} meter candle seconds exposure, the combination developer produced 10 μg of silver/cm² while no detectable silver was developed by a developer containing only one of the two developing agents. These data illustrate the synergistic effect produced when my phenolic developing agents are used with a developing agent (a) identified above for negative development.

Similar results are obtained when Example 1 is repeated using other of my phenolic silver halide developing agents of Formulas I and II in place of 2,4-bis(benzenesulfonamido)phenol. In such combination developers, the useful concentration for my developing agents is in the range of from about 5 to about 20 grams per liter, with a preferred concentration in the range from about 8 to about 15 grams per liter. The other non-color-forming silver halide developing agent (a) in my compositions is advantageously used in the range of from about 1 to 15 grams per liter, and in the preferred range of from about 5 to 10 grams per liter.

The following example will illustrate the use of my phenolic developing agents as competing developing agents in compositions for making color developer solutions.

EXAMPLE 2

A composition for preparing a cyan color developing solution was made comprising 2.05 grams of 4-amino-N-ethyl-N-beta-hydroxyethyl-3-methylaniline sulfate and 2 grams of 2,4-bis(benzenesulfonamido)phenol. This dry composition was used to make a cyan color developer solution by dissolving it in 1 liter of a solution containing 1.65 grams of the cyan-forming coupler; 2-(o-acetamido-beta-phenylethyl)-1-hydroxynaphthamide; 2 grams of sodium sulfite; 2½ grams of sodium bromide and 1 gram of sodium thiocyanate that had been adjusted to a pH of 12.4.

A multilayer, color film of the type adapted to be exposed in the usual manner in reversal processing, first in a black-and-white negative developer, followed by reversal reexposures and development in appropriate color developers containing the color couplers or color-formers, was exposed to a colored object and then processed as described in Example 2 of Bard et al. U.S. Pat. No. 3,141,771, issued July 21, 1964, except that the above-described cyan developer was used in place of the cyan developer described in that patent. The magenta and yellow developers were identical to the magenta and yellow developers of that patent. A suitable color film for such processing is desribed in Mannes et al U.S. Pat. No. 2,252,718, issued Aug. 19, 1941. Such a film yielded an excellent reproduction of the original and examination of the processed film showed good color reproduction with cyans free of unwanted green absorption and with high-light densities free of unwanted cyan dye. Sensitometric (i.e., graphs of color

density v. log exposure) plotted for the cyan, yellow and magenta dyes prepared from density measurements showed desirable reductions of cyan dye in the D-min. portions of the sensitometric curves, while the cyan D-max. remained at the desired level. After prolonged use, my cyan color developers remained free of the tacky dirt which is characteristically formed with prior art cyan developer solutions containing MBAP.

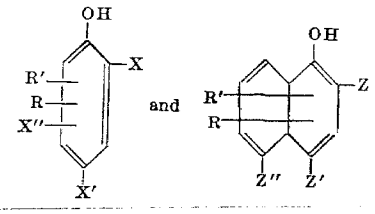
Similar results can be obtained using compositions containing from about 0.5 to about 10 grams per liter of the color developing agent used in Example 2 (or other primary aromatic amine color developing agents) and varying amounts of a phenolic competing developing agent of Formula I or II in the range of from about 0.1 to about 2 grams per liter. Similar results are also obtained when my phenolic silver halide developing agents are used as competing (or balancing) developers in the cyan, yellow and magenta color developers, or in other color processes where competing developing agents are needed. My phenolic silver halide developing agents are also used advantageously as competing developing agents in color developer solutions that do not contain color-forming couplers and are used for color developing color photographic materials that contain incorporated couplers either in differently sensitized silver halide emulsion layers of multilayer materials, or in single layer materials containing three differently sensitized packets that contain the appropriately sensitized silver halide emulsion with the appropriate color-forming couplers. In addition to this, my developing agents are also used advantageously together with a second non-color-forming silver halide developing agent (a) in the negative (black-and-white) developer used in reversal color processes. The optimum concentrations for the developing agents will depend upon the particular developers used, the other components in the developer, and other solutions used in the process, the processing conditions, characteristics of the photographic material to be processed, etc., and are determined by methods well known in the art.

The developers of my invention represented by formulas I and II above can also be incorporated in the viscous developing solutions used in color diffusion transfer processes, such as that described in Weyerts et al U.S. Pat. No. 3,266,894, issued Aug. 16, 1966. The developers of my invention can be used in whole or in part to replace the hydroquinone-type developer (MPHQ) used in the process of that patent.

The invention has been described in detail with particular embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A silver halide developing agent selected from compounds having one of the formulas:



wherein X represents a $-N^{L}SO_2Q$ group; X' represents a $-N^{L'}SO_2Q'$ group; X'' represents a member of the class consisting of hydrogen and a $-N^{L}SO_2Q$ group; L and L' each represents a member of the class consisting of hydrogen, methyl, ethyl, propyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, hydroxypropyl, hydroxybutyl; Q and Q' each represents a member of the class consisting of methyl, ethyl, butyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, benzyl, phenethyl, octyl, phenyl, 4-carboxyphenyl, 4-sulfophenyl, 2-ethoxyphenyl, 4-methylphenyl, 2-chlorophenyl, 4-nitrophenyl, α-naphthyl, β-naphthyl, 4-carboxynaphthyl, 4-sulfonaphthyl; R and R' each represents a member of the class consisting of hydrogen, methyl, ethyl, propyl, sulfoethyl, sulfobutyl, carboxymethyl, carboxypropyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, methoxy, ethoxy, propoxy, acetyl, butyryl, benzoyl, 4-methylbenzoyl, halogen, and cyano; Z represents a member of the class consisting of hydrogen and a $-N^{L}SO_2Q$ group; Z' represents a member of the class consisting of hydrogen and a $-N^{L}SO_2Q'$ group; Z'' represents a member of the class consisting of hydrogen and a $-N^{L}SO_2Q$ group; with the proviso that at least two of Z, Z' and Z'' are not hydrogen.

2. 2,5-Bis(benzenesulfonamido)-1-naphthol.

3. 2,4-Bis(benzenesulfonamido)phenol.

4. 2,4-Bis(methanesulfonamido)-5-methylphenol.

5. 2-Methanesulfonamido-4-benzenesulfonamidophenol.

6. 2,4-Bis(N-methyl-benzenesulfonamido)-5-sulfophenol.

* * * * *