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SULFONAMIDE SUBSTITUTED P-PHENYLENEDIAMINES CONTAINING O-ALKOXY GROUPS AS SILVER HALIDE PHOTOGRAPHIC DEVELOPERS

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11 Claims. (Cl. 95—88)

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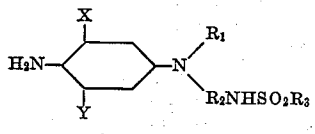
This invention relates to photographic developers and more particularly to photographic developers of the substituted p-phenylenediamine type.

This application is a continuation-in-part of application Serial No. 654,528, filed March 14, 1946, now abandoned.

It is known that p-phenylenediamine photographic developers are valuable compounds for producing fine grain black-and-white photographic images, and also, that these compounds, especially when they contain alkyl substituents, are useful as developers in processes for producing colored photographic images. The phenylenediamine developers, however, have several defects. A common difficulty encountered when using these developers is their low activity and the low contrast and emulsion speed obtained with them. Other disadvantages are their low solubility in developing solutions and their allergenic character, that is, their poisonousness to the human skin. These latter defects have been solved, according to Weissberger U. S. Patent 2,193,015, by adding a sulfonamide group to one of the nitrogen atoms of p-phenylenediamine. Developers of this type, however, exhibit low developing activity.

A principal object of the present invention is, therefore, to provide new developing agents of the substituted p-phenylenediamine type having high developing activity and which are capable of giving high contrast and emulsion speed.

We have discovered that the rate of development with sulfonamide substituted p-phenylenediamines is remarkably increased by substituting an alkoxy group in the benzene ring in ortho position with respect to the primary amino group. These novel compounds have the following general formula:



wherein X represents a member selected from the group consisting of hydrogen, alkyl groups, alkoxy groups, and substituted alkoxy groups; Y represents a member selected from the group consisting of alkoxy groups and substituted alkoxy groups; R_1 represents a member selected

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from the group consisting of hydrogen, alkyl groups, and substituted alkyl groups; R_2 represents an alkylene radical selected from the group consisting of ethylene and propylene; and R_3 represents a member selected from the group consisting of alkyl groups and hydrogen.

Specific compounds which we contemplate using include:

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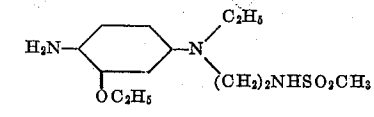

4-amino-3-ethoxy-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline

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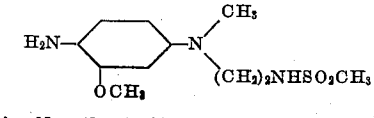

4-amino-N-methyl-N-(β-methylsulfonamidoethyl)-m-anisidine

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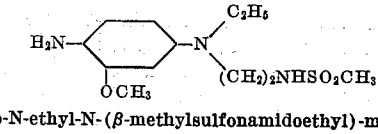

4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)-m-anisidine

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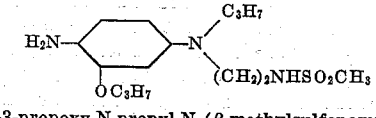

4-amino-3-propoxy-N-propyl-N-(β-methylsulfonamidoethyl)-aniline

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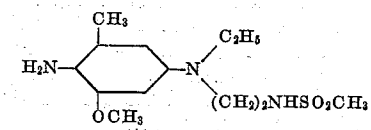

4-amino-3-methoxy-5-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline

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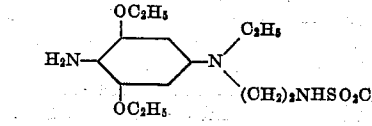
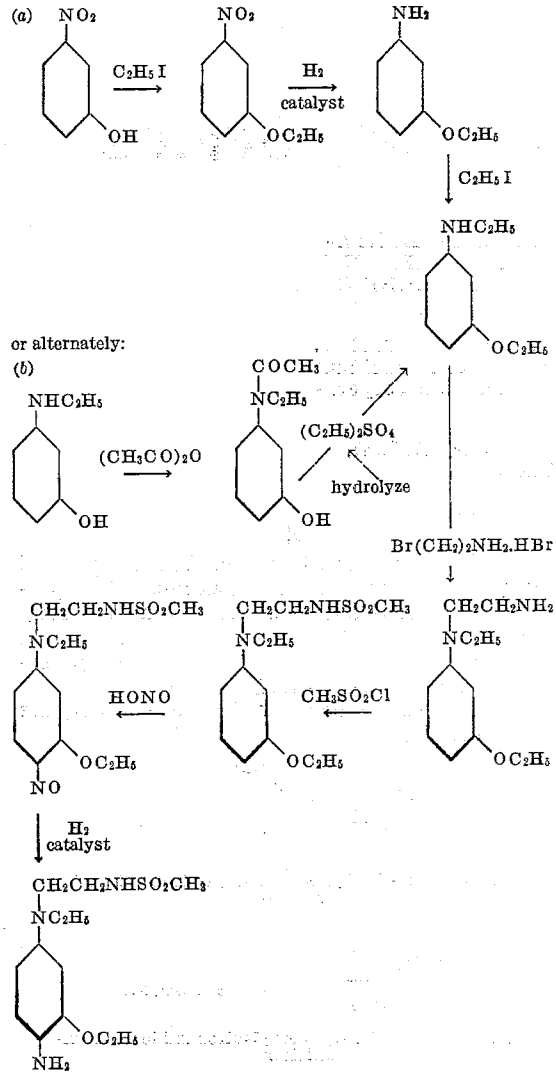


4-amino-3,5-diethoxy-N-(β-methylsulfonamidoethyl)-aniline

The preparation of these compounds is illustrated by the preparation of 4-amino-3-ethoxy-N - ethyl - N - (β - methylsulfonamidoethyl)-

aniline, which may be synthesized by the following methods:



The preparation of 4-amino-N-ethyl-N-(β-methylsulfonamido-ethyl)-m-phenetidine (Compound 1) may be illustrated by the following procedure:

N-ethyl-m-acetophenetide.—A mixture of one mole of m-phenetidine and one mole of ethyl iodide was warmed in a waterbath to 40° at which temperature an exothermic reaction began. The temperature was allowed to rise to 60° and then was maintained at this temperature for one hour first by cooling and as the exothermic reaction subsided by warming. After standing overnight, the reaction mixture was stirred with 200 ml. of water and 100 ml. of 40% caustic until all of the solid had gone into solution. The amines were extracted with ether, the ethereal solution was dried over solid sodium hydroxide and the ether was evaporated. The residue was added to 100 g. of acetic anhydride with stirring and cooling so that the temperature did not rise above 50°. This mixture was heated on the steam bath for thirty minutes, cooled and then stirred with 150 ml. of water until all of the excess anhydride had decomposed. The mixture was made alkaline with 40% caustic solution and the product was extracted with ether. The ethereal solution was dried over solid sodium sulfate and the ether was evaporated. The residue was distilled under reduced pressure collecting the portion that boiled at 105–110°/1 mm. as the desired product. The yield was 80 per cent.

N-ethyl-m-phenetidine.—One mole of N-ethyl-m-acetophenetide was boiled with 150 ml. of water and 150 ml. of concentrated hydrochloric acid for six hours. The reaction mixture was cooled, made alkaline with 200 ml. of 40% caustic solution and the amine was extracted with ether. The ethereal solution was dried over solid sodium hydroxide and the ether was evaporated. The residue was distilled under reduced pressure collecting the portion that boiled at 148–150°/17 as the desired product. The yield amounted to 90 per cent.

N-(β-aminoethyl)-N-ethyl-m-phenetidine.—A mixture of 1 mole of N-ethyl-m-phenetidine and 0.5 mole of β-bromoethylamine hydrobromide was stirred and heated at 140–150° for two and one-half hours. At the end of this time the reaction mixture was cooled and 225 ml. of water and 75 ml. of 40% caustic solution were added. After all of the organic salts had dissolved, the product was extracted with ether. The ethereal solution was dried over solid sodium hydroxide and the ether was evaporated. The residue was distilled under reduced pressure collecting the portion that boiled at 157–160°/6 mm. as the desired product. The yield was 80 per cent.

N-ethyl-N-(β-methylsulfonamidoethyl)-m-phenetidine.—A mixture of 0.625 mole of N-(β-aminoethyl)-N-ethyl-m-phenetidine and 250 ml. of water was stirred vigorously, and 80 g. (0.7 mole) of methane-sulfonyl chloride was added during a period of 30 minutes, the temperature of the reaction mixture being kept at 15±5° during the addition of the chloride. After each quarter of the acid chloride had been admitted, one-fourth of a solution of 28 g. (0.7 mole) of sodium hydroxide in 75 ml. of water was introduced. The mixture was then stirred for two hours at 20–25° and made alkaline with ammonium hydroxide. The amide was extracted with chloroform, the chloroform solution was washed with water and dried over sodium sulfate. The chloroform was evaporated under reduced pressure. The residue of crude amide amounted to 90 per cent.

N-ethyl-N-(β-methylsulfonamidoethyl)-4-nitroso-m-phenetidine.—One half mole of N-ethyl-N-(β-methylsulfonamidoethyl)-m-phenetidine was dissolved in a mixture of 140 ml. of concentrated hydrochloric acid and 500 ml. of hot water. This solution was cooled quickly to 5° and maintained at this temperature while a solution of 39 g. (0.56 mole) of sodium nitrite in 50 ml. of water was added, with stirring, during a period of 20 minutes. After standing at 5° for one hour, the reaction mixture was made alkaline with ammonium hydroxide. The precipitate was filtered with suction and washed with water. The moist produce was recrystallized twice from 500 ml. portions of 3-A alcohol and dried in air. The yield was 85 per cent.

4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)-m-phenetidine oxalate.—One-half mole of N-ethyl-N-(β-methylsulfonamidoethyl)-4-nitroso-m-phenetidine was dissolved in 500 ml. of absolute alcohol and reduced in the presence of Raney nickel at a hydrogen pressure of 45 lbs./in.^{2} and a temperature of 60°. After the reduction was complete, the catalyst was filtered off and 0.5 mole of powdered, anhydrous oxalic acid was added. The mixture was warmed until all of the oxalic acid had dissolved and then was cooled to 0° and allowed to stand until crystallization was

complete. The crystals were filtered off, washed with absolute alcohol and dried in a vacuum desiccator over sulfuric acid. The yield was 80 per cent.

4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)-m-anisidine (Compound 3), 4-amino-3,5-diethoxy-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline (Compound 6) and 4-amino-3-methoxy-5-methyl-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline (Compound 5) can be prepared by this procedure from m-anisidine, 3,5-diethoxyaniline and 3-methoxy-5-methylaniline respectively.

4-amino-N-methyl-N-(β-methylsulfonamidoethyl)-m-anisidine (Compound 2) can be prepared from m-anisidine and 4-amino-3-propoxy-N-propyl-N-(β-methylsulfonamidoethyl)-aniline (Compound 4) from 3-propoxyaniline by this procedure if instead of using ethyl iodide in the first step of the syntheses, methyl iodide is used for the first compound and propyl iodide is used for the second.

The introduction of more than one ethoxy group in the ortho positions with respect to the primary amino group as well as the introduction of an alkyl group in one ortho position and an alkoxy group in the other must be considered part of the present invention. Instead of ethoxy groups, other alkoxy groups may be used, including alkoxy groups with additional substituents in the aliphatic radical, such as OH, Cl, OR, etc.

When used for the formation of colored photographic images, the developers of our invention may be used in conjunction with any well known coupler compounds such as those described in Fischer U. S. Patent 1,102,028, June 30, 1914; Mannes and Godowsky U. S. Patent 2,108,602, February 15, 1938; Mannes, Godowsky and Peterson U. S. Patent 2,115,934, April 26, 1938; and Mannes, Godowsky and Peterson U. S. Patent 2,126,337, August 9, 1938.

The following examples, which are illustrative only, indicate developing solutions which may be used according to our invention.

Example 1

A

4-amino-3-ethoxy-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline	grams	1
Sodium sulfite	do	0.5
Sodium carbonate	do	20
Water to	cubic centimeters	1000

B

Coupler	grams	1
Acetone	cubic centimeters	50

Add B to A

Example 2

For the formation of a fine grain black-and-white image, the following developing solution may be used:

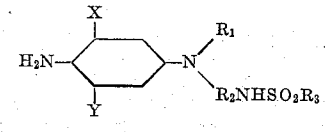
4-amino-N-ethyl-N-(β-methylsulfonamidoethyl)-m-anisidine	grams	5
Sodium sulfite	do	30
Sodium carbonate	do	30
Water to	cubic centimeters	1000

While we have given numerous examples of compounds illustrating our invention, it is obvious that various modifications can be made without departing from the spirit thereof. The specific alkoxy and alkyl substituents may be varied and different combinations of these substituents may be employed. Although these compounds are of particular value as photographic developers, they have other utility as in the dyeing of fur and hair.

Having thus described our invention, what we now claim and desire to secure by U. S. Letters Patent is:

1. A developing solution for producing a colored photographic image comprising as a silver halide developing agent, a 4-amino-3-alkoxy-N-(β-alkylsulfonamidoalkyl)-aniline, and a compound which couples with the oxidation product of said developing agent at the primary amino group to form a colored image on development.

2. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing a compound of the following general formula:



wherein X represents a member selected from the group consisting of hydrogen, alkyl groups, alkoxy groups and substituted alkoxy groups; Y represents a member selected from the group consisting of alkoxy groups and substituted alkoxy groups; R_1 represents a member selected from the group consisting of hydrogen, alkyl groups and substituted alkyl groups; R_2 represents an alkylene radical selected from the group consisting of ethylene and propylene; and R_3 represents a member selected from the group consisting of alkyl groups and hydrogen, for a sufficient time to develop the latent image to a visible silver image.

3. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing a p-phenylenediamine having an alkoxy substituent in the ortho position with respect to the primary nitrogen atom of the p-phenylenediamine and a sulfonamidoalkyl substituent attached to the secondary nitrogen atom of the p-phenylenediamine, for a sufficient time to develop the latent image to a visible silver image.

4. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing a 4-amino-3-alkoxy-N-alkyl-N-(β-alkylsulfonamidoalkyl)-aniline, for a sufficient time to develop the latent image to a visible silver image.

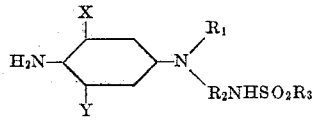
5. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing a 4-alkyl-N-(β-alkylsulfonamidoalkyl)-aniline, for a sufficient time to develop the latent image to a visible silver image.

6. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing a 4-amino-3-alkoxy-5-alkyl-N-alkyl-N-(β-alkylsulfonamidoalkyl)-aniline, for a sufficient time to develop the latent image to a visible silver image.

7. The method of developing a silver halide emulsion which comprises treating an exposed silver halide emulsion layer containing a latent image, with a solution containing 4-amino-3-ethoxy-N-ethyl-N-(β-methylsulfonamido-

ethyl)-aniline, for a sufficient time to develop the latent image to a visible silver image.

8. A developing solution for producing a colored photographic image comprising as a silver halide developing agent a compound of the following general formula:



wherein X represents a member selected from the group consisting of hydrogen, alkyl groups, alkoxy groups and substituted alkoxy groups; Y represents a member selected from the group consisting of alkoxy groups and substituted alkoxy groups; R_1 represents a member selected from the group consisting of hydrogen, alkyl groups and substituted alkyl groups; R_2 represents an alkylene radical selected from the group consisting of ethylene and propylene; and R_3 represents a member selected from the group consisting of alkyl groups and hydrogen, and a compound which couples with the oxidation product of said developing agent at the primary amino group to form a colored image on development.

9. A developing solution for producing a colored photographic image comprising as a silver halide developing agent a 4-amino-3,5 dialkoxy-N-alkyl-N-(β-alkylsulfonamidoalkyl)-aniline and a compound which couples with the oxidation product of said developing agent at the primary amino group to form a colored image on development.

10. A developing solution for producing a colored photographic image comprising as a silver halide developing agent a 4-amino-3-alkoxy-5-alkyl-N-alkyl-N-(β-alkylsulfonamidoalkyl)-aniline and a compound which couples with the oxidation product of said developing agent at the primary amino group to form a colored image on development.

11. A developing solution for producing a colored photographic image comprising as a silver halide developing agent 4-amino-3-ethoxy-N-ethyl-N-(β-methylsulfonamidoethyl)-aniline and a compound which couples with the oxidation product of said developing agent at the primary amino group to form a colored image on development.

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DUDLEY B. GLASS.
PAUL W. VITTUM.

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