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P-PHENYLENEDIAMINE DEVELOPER CONTAINING N-ALKYLACETAMIDO ETHYL SUBSTITUENT

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4 Claims. (Cl. 95—88)

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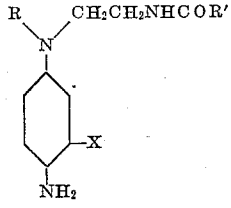
This invention relates to photographic developers and more particularly to photographic developers containing an N-alkyl acetamido ethyl substituent.

It is known that photographic developers of the p-phenylenediamine type are valuable compounds for producing fine grain black and white photographic images and also that these compounds, especially when they contain alkyl substituents on one of the nitrogen atoms, are useful as developers in producing colored photographic images. A serious disadvantage of the p-phenylenediamine developers is that they are highly allergenic, that is, they are poisonous to the human skin and are therefore somewhat dangerous to use.

The allergenic properties of the p-phenylenediamine developers may be overcome by substituting a sulfonamide group or an amino sulfonyl group in the alkyl group on the nitrogen atom of p-phenylenediamine as described in Weissberger U. S. Patent 2,193,015, granted March 12, 1940. The substituted p-phenylenediamine developing agents are, however, sometimes too low in developing strength (reduction potential) so that it is difficult to obtain, with them, dye images of sufficiently high density and contrast.

It is therefore an object of the present invention to provide a new class of photographic developing agents of the p-phenylenediamine type. A further object is to provide developing agents of the p-phenylenediamine type which produce dye images having the desired characteristics.

These objects are accomplished by the present invention by the use as developing agents of compounds having the following general formula:

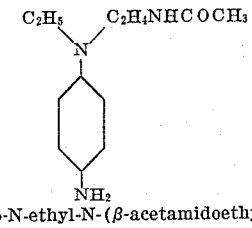


where R is a lower alkyl group such as methyl, ethyl, or propyl, R' is a lower alkyl group and X is hydrogen, a lower alkyl group or a lower alkoxy group.

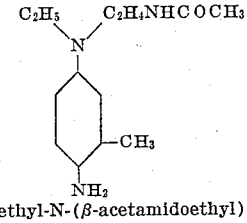
By "lower alkyl" group, we mean a methyl, ethyl or propyl group. By "lower alkoxy" group we mean a methoxy, ethoxy or propoxy group.

Compounds of this class which may be used according to our invention are as follows:

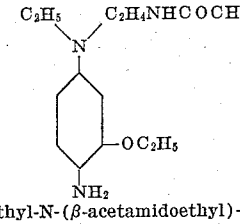
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4-amino-N-ethyl-N-(β-acetamidoethyl)-aniline

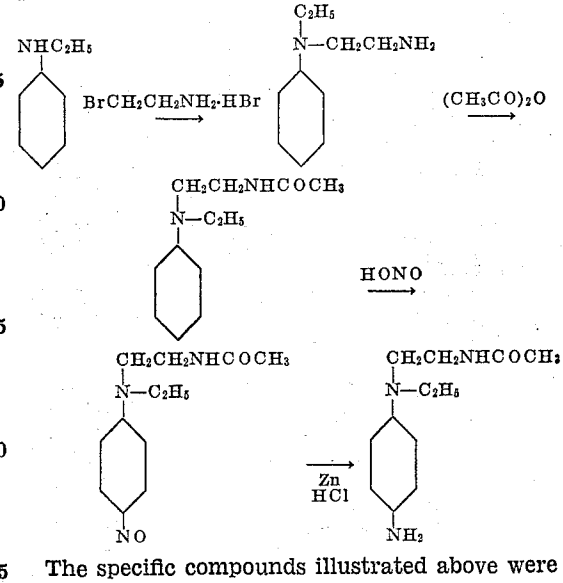


4-amino-N-ethyl-N-(β-acetamidoethyl)-m-toluidine



4-amino-N-ethyl-N-(β-acetamidoethyl)-m-phenetidine

The preparation of our developers may be summarized by the following reaction scheme which indicates the general method used in preparing compound 1.



The specific compounds illustrated above were prepared as follows:

Compound 1, [4-amino-N-ethyl-N-(β-acetami-

doethyl)-aniline], was prepared from N-ethylaniline by the following series of reactions:

(*a*) *N-(β-aminoethyl)-N-ethylaniline.*—A mixture of N-ethylaniline (2 moles) and (β-bromoethylamino hydrobromide (1 mole) was placed in a flask in an oil bath and the temperature of the oil bath was raised to 145–150° C. during 45 minutes. The reaction mixture was stirred at this temperature for 2 hours, cooled, diluted with water, and made alkaline with 40% sodium hydroxide solution. The amine was extracted with ether, the ether solution was washed with water and the ether was evaporated. The residue was distilled under reduced pressure. The fraction that boiled at 120–122° at 6 mm. was collected.

(*b*) *4-amino-N-ethyl-N-(β-acetamidoethyl)-aniline.*—N-(β-aminoethyl)-N-ethylaniline (1 mole) was added to 105 ml. of acetic anhydride with stirring and cooling so that the temperature did not rise above 80°. The solution was then heated at 100° for 30 minutes and diluted with 500 ml. of water. The mixture was acidified with 250 ml. of concentrated hydrochloric acid and stirred until solution took place. After cooling to 0°, the amine was nitrosated by the addition of a solution of 70 g. of sodium nitrite in 150 ml. of water during a period of 30 minutes. The solution was stirred at 0–5° for 15 minutes then further acidified by the addition of 200 ml. of concentrated hydrochloric acid. This solution was maintained at 10±5° and 135 g. of zinc dust was added in small portions during the course of 1 hour. The colorless solution was filtered to remove the excess zinc and made alkaline with 1 l. of ammonium hydroxide. The diamine was extracted with chloroform. The chloroform solution was washed with water and dried over anhydrous sodium sulfate. The chloroform was distilled at atmospheric pressure and the diamine was distilled under reduced pressure. The portion that boiled at 204–206° at 2 mm. was collected.

Compound 2, [4-amino-N-ethyl-N-(β-acetamidoethyl)-m-toluidine], and Compound 3, [4-amino-N-ethyl-N-(β-acetamidoethyl)-m-phenetidine], were prepared from N-ethyl-m-toluidine and N-ethyl-m-phenetidine, respectively, by the same procedure used to prepare Compound 1 from N-ethylaniline.

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 Fisher U. S. Patent 1,102,028, granted June 30, 1914, Mannes and Godowsky U. S. Patent 2,108,602, granted February 15, 1938, or Mannes, Godowsky and Peterson U. S. Patent 2,115,394, granted April 26, 1938 and 2,126,337, granted August 9, 1938.

The following example illustrates a developing solution which may be used according to our invention.

(*a*) 4-amino-N-ethyl-N-(β-acetamidoethyl) aniline	grams	1
Sodium sulfite	do	2
Sodium carbonate	do	30
Potassium bromide	do	2
Water to 1 liter.		
(*b*) Coupler (2,4-dichloro-1-naphthol)	grams	2
Sodium hydroxide (10% solution)	cc.	20

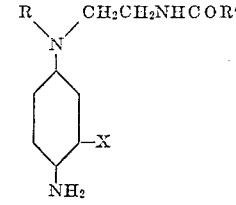
For use (*b*) is added to (*a*).

The developing agents described in the present application may be used to form photographic images by development of exposed silver halide contained in the usual gelatin carrier or in carriers such as collodion, water-permeable cellulose ester or water-permeable synthetic resin. Our developing agents may be used with photographic films containing the coupler in the emulsion layer as described in Mannes and Godowsky U. S. Patent 2,304,940, granted December 15, 1942, or Jelley and Vittum U. S. Patent 2,322,027, granted June 15, 1943. When used in this way, a developing solution similar in composition to part (*a*) in the above example is suitable.

It will be understood that the examples of modifications included herein are illustrative only.

We claim:

1. A silver halide developing solution for producing a colored photographic image comprising a developing agent having the general formula:



where R is a lower alkyl group, R' is a lower alkyl group and X is selected from the class consisting of hydrogen, lower alkyl and lower alkoxy groups, and a compound which couples with the oxidation product of said developing agent to form a colored image upon photographic development.

2. A silver halide developing solution for producing a colored photographic image comprising a substantial amount of 4-amino-N-ethyl-N-(β-acetamidoethyl) aniline, and a compound which couples with the oxidation product of said developing agent upon development to form a colored image.

3. A silver halide developing solution for producing a colored photographic image comprising a substantial amount of 4-amino-N-ethyl-N-(β-acetamidoethyl)-m-toluidine, and a compound which couples with the oxidation products of said developing agent upon development to form a colored image.

4. A silver halide developing solution for producing a colored photographic image comprising a substantial amount of 4-amino-N-ethyl-N-(β-acetamidoethyl)-m-phenetidine, and a compound which couples with the oxidation products of said developing agent upon development to form a colored image.

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