

UNITED STATES PATENT OFFICE

2,298,443

NONDIFFUSING SULPHONAMIDE COUPLER
FOR COLOR PHOTOGRAPHYArnold Weissberger, Rochester, N. Y., assignor to
Eastman Kodak Company, Rochester, N. Y., a
corporation of New JerseyNo Drawing. Application August 22, 1940, Serial
No. 353,669. In Great Britain August 24, 1939

3 Claims. (Cl. 95-6)

This invention relates to photographic color forming compounds and particularly to non-diffusing coupler compounds containing sulphonamide groups for incorporation in photographic emulsion layers.

Color forming compounds which react with the development product of aromatic amino developing agents to form colored images on photographic development have been the subject of numerous prior patents. The dyes formed in this way are insoluble in water and in the ordinary photographic developing and fixing baths although the silver images formed simultaneously with them during the photographic development may be removed from the photographic layer to leave pure dye images in the layer. Such a compound which is employed in conjunction with the developing agent for the silver and which couples with the development product of the developer during photographic development is referred to herein as a coupling component or coupler. When these coupling components are incorporated in the photographic layer prior to exposure, they do not affect the exposure and development of the layer in the usual way but when the development is carried out with a suitable developing agent they combine with the oxidation product of the developer to form a colored image in situ with the silver image.

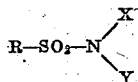
In Vittum, Peterson and Porter U. S. Patent No. 2,271,238, granted January 27, 1942, coupling components are described which contain sulphonamide groups. Such couplers are desirable by reason of their solubility characteristics and the improved properties of the dyes formed from them. The couplers described in the Vittum, Peterson and Porter application are, in general, soluble in the developing solution and not suitable for use in the emulsion layer because of their tendency to diffuse from the layer. The dyes formed from these couplers, however, have better light transmission characteristics and are more stable to heat and light than the dyes produced from previously known coupling components.

It is an object of the present invention to provide coupling components which have the desirable properties of couplers containing the sulphonamide group but which may be incorporated in photographic emulsion layers as non-diffusing compounds. A further object is to provide novel photographic couplers having desirable properties with respect to heat and light stability. A still further object is to provide photographic couplers which form image dyes having desirable light transmission characteristics.

Other objects will appear from the following description of my invention.

These objects are accomplished by replacing the free hydrogen atom of the sulphonamide group of couplers containing such group with radicals having the property of rendering the couplers non-diffusing in gelatin or other colloidal media.

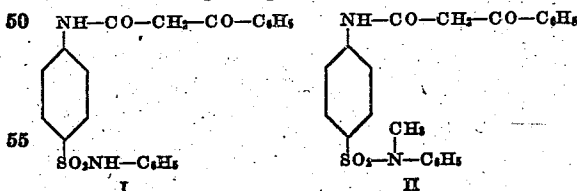
The color forming or coupling compounds which I have found to be suitable for incorporation in silver halide emulsion layers according to my invention are compounds having the general structure



where R is an aryl radical such as phenyl or naphthyl which may be substituted but which may not be a hydroxy substituted aryl radical, X is an alkyl or phenyl substituted alkyl which may be substituted and Y is an organic substituent such as alkyl or aryl radicals.

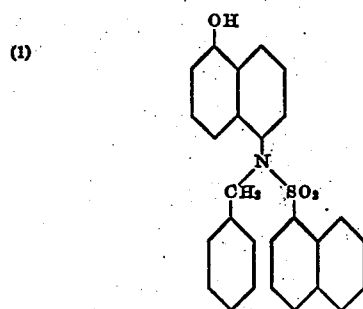
The coupler must also contain a group reactive with the oxidation product of the developer to form a dye. This group is the reactive methylene or ethenol group characteristic of coupler compounds and will be more specifically referred to hereinafter. In the case of a reactive methylene group, it may be contained in the portion of the molecule attached either to the sulphur or to the nitrogen atom of the sulphonamide group. In the case of the reactive ethenol group this group may not be attached directly to the sulphur atom of the sulphonamide but may be attached to the nitrogen atom or to one of the groups attached to the nitrogen atom of the sulphonamide radical. As pointed out in the Vittum, Peterson and Porter Patent No. 2,271,238, couplers having the reactive ethenol group attached to the sulphur atom of the sulphonamide produce dyes which are less stable to heat and light than compounds having the ethenol group attached to the nitrogen atom of the sulphonamide group or having a reactive methylene group attached either to the sulphur atom or to the nitrogen atom.

My invention may be illustrated by reference to the following compounds I and II.

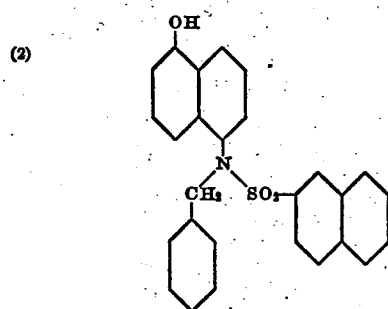


Compound I is a coupler capable of producing a yellow dye image and is of the type described in Vittum, Peterson and Porter U. S. Patent No. 2,271,238. It is soluble in photographic developing solutions. Compound II is identical with compound I except that the free hydrogen atom of the sulphonamide group has been replaced with a methyl radical. Compound II also produces a yellow dye upon development with the proper photographic developing agent. However, because of the replacement of the hydrogen atom of the sulphonated group with a suitable radical, the coupler is no longer soluble in the developer but may be incorporated in a photographic emulsion layer as a non-diffusing compound. My invention resides in the discovery that, by the substitution of this free hydrogen atom of the sulphonamide group with suitable organic radicals, the valuable properties of the sulphonamide couplers may be retained, but the solubility properties of the coupler are materially altered and the coupler is rendered non-diffusing in gelatin or other colloidal media.

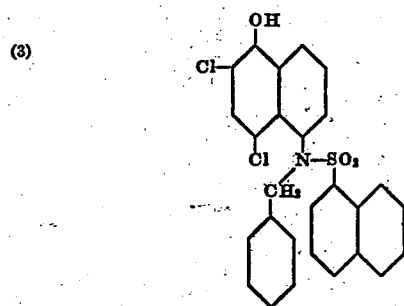
Compounds suitable for use as non-diffusing couplers according to my invention are as follows:



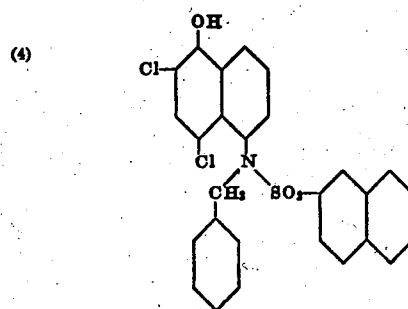
5-[N-(benzyl)-α-naphthalene-sulphonylamino]-1-naphthol



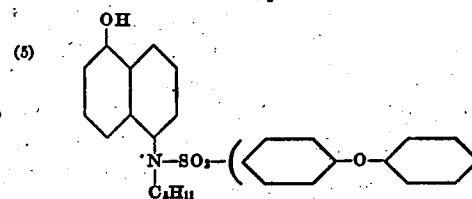
5-[N-(benzyl)-β-naphthalene-sulphonylamino]-1-naphthol



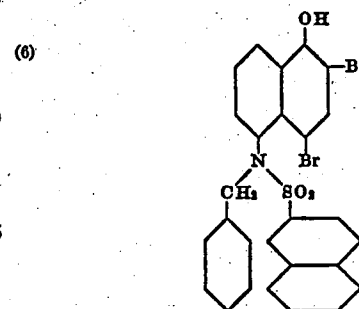
2,4-dichloro-5-[N-(benzyl)-α-naphthalene-sulphonylamino]-1-naphthol



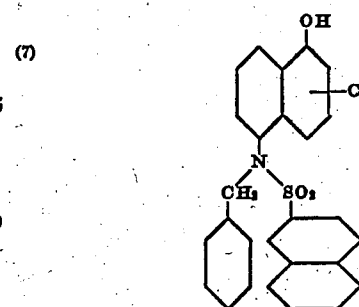
2,4-dichloro-5-[N-(benzyl)-β-naphthalene-sulphonylamino]-1-naphthol



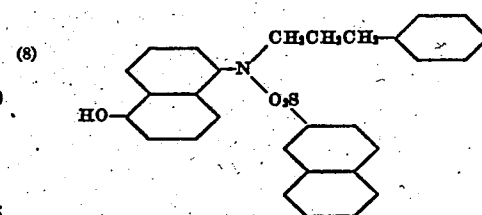
5-amyldiphenylethersulphonylamino-1-naphthol



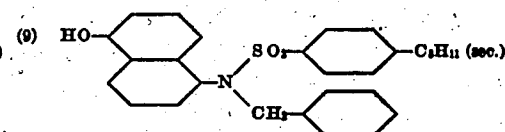
2,4-dibromo-5-[N-(benzyl)-β-naphthalene-sulphonylamino]-1-naphthol



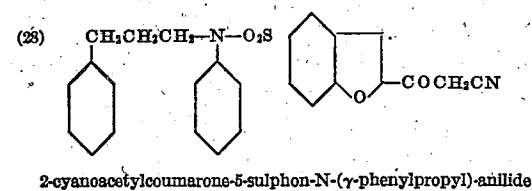
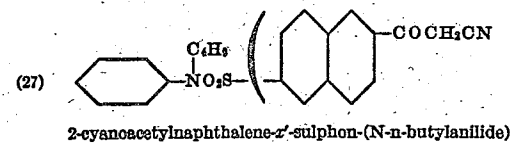
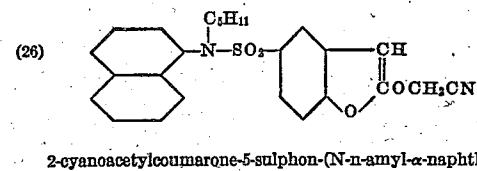
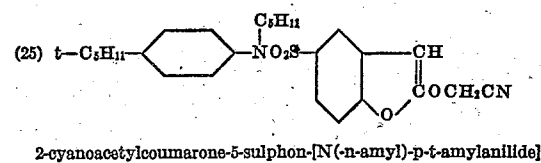
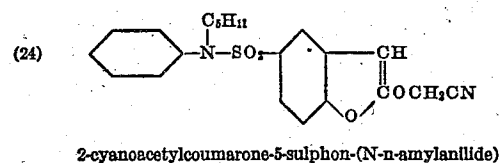
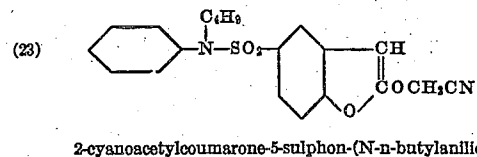
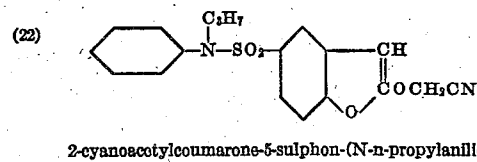
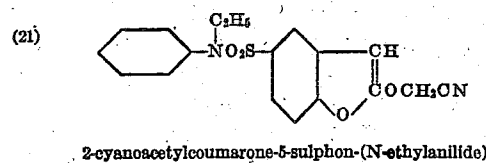
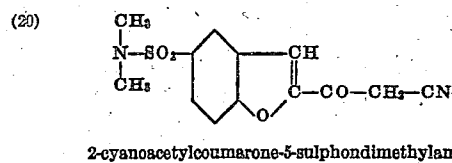
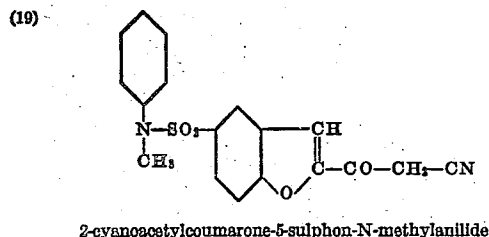
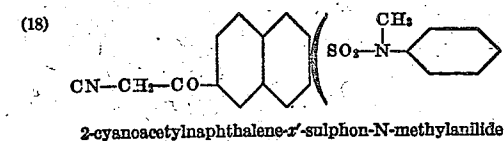
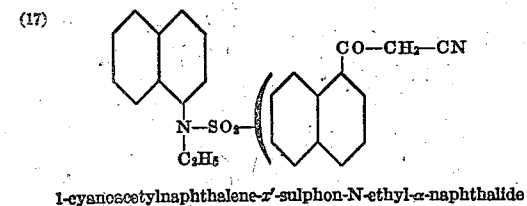
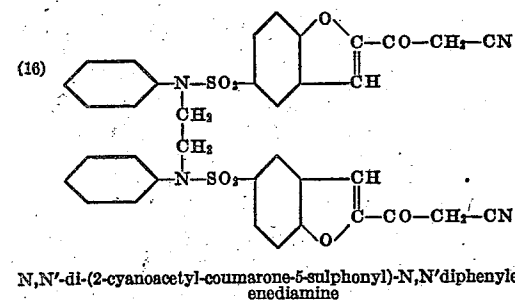
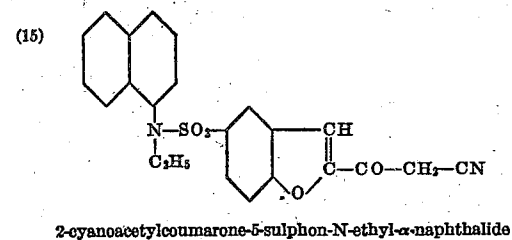
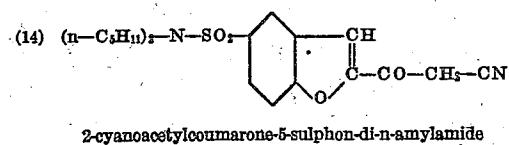
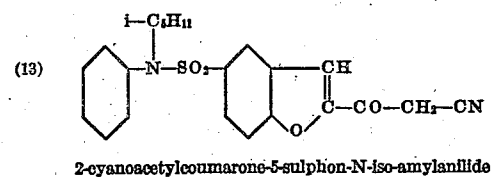
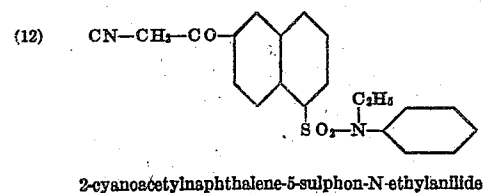
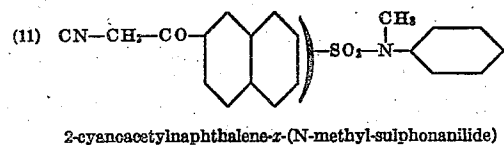
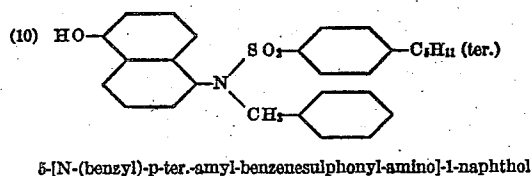
α-monochloro-5-[N-(benzyl)-β-naphthalene-sulphonylamino]-1-naphthol

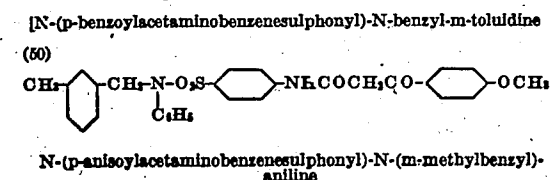
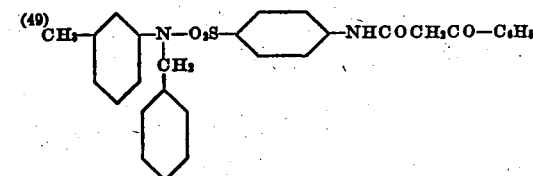
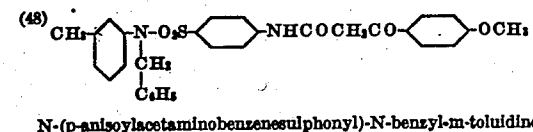
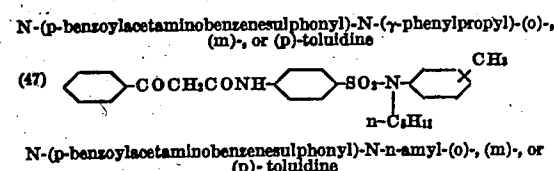
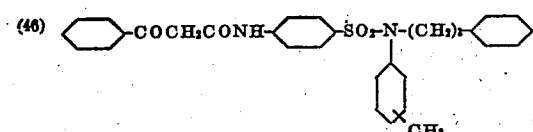
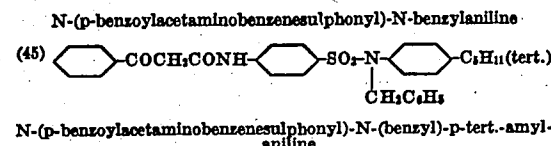
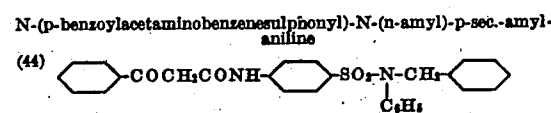
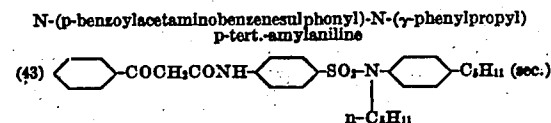
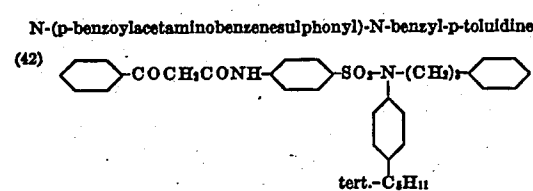
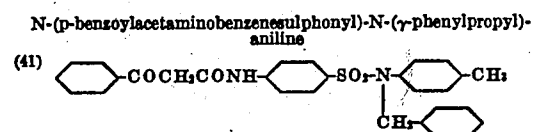
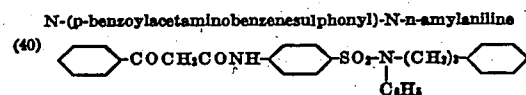
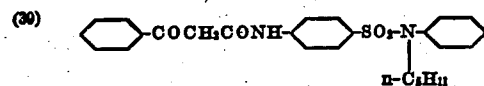
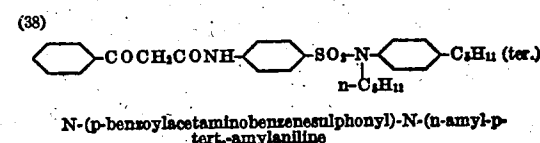
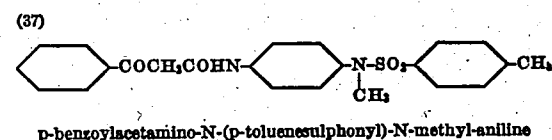
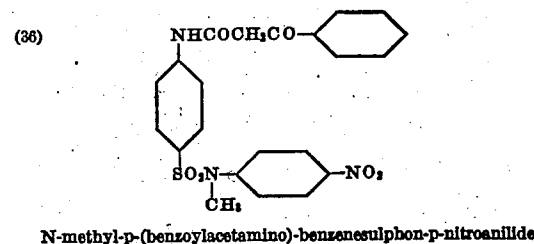
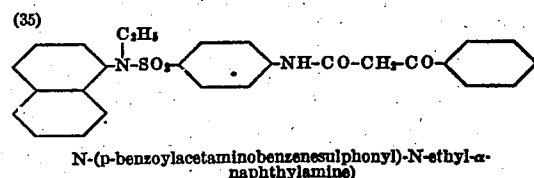
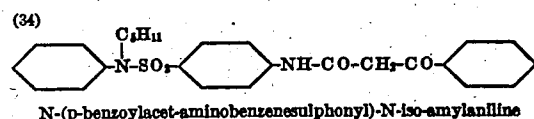
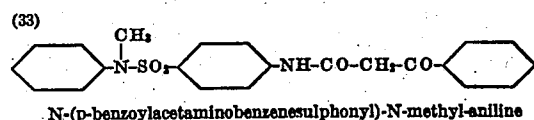
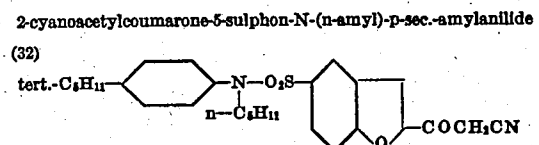
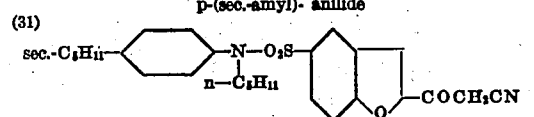
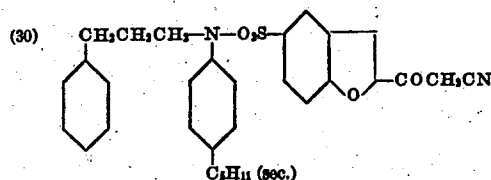
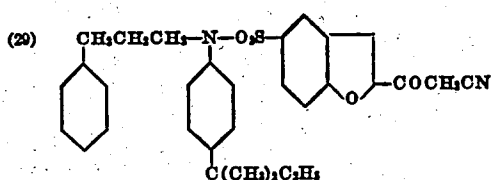


5-[N-γ-(phenylpropyl)-4-naphthalene-sulphonylamino]-1-naphthol (and α-monochloro derivative)

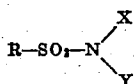


5-[N-(benzyl)-p-sec-amyli-benzenesulphonylamino]-1-naphthol



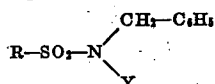


containing a sensitive silver halide and a coupler compound having the formula:



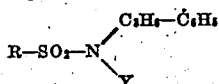
where R is an aryl radical other than a hydroxy substituted aryl radical, X is a phenyl substituted alkyl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developers.

2. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and a coupler compound having the formula:



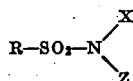
where R is an aryl radical other than a hydroxy substituted aryl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with aromatic amino developers.

3. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and a coupler compound having the formula:



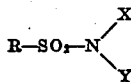
where R is an aryl radical other than a hydroxy substituted aryl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with aromatic amino developers.

4. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and a coupler compound having the formula:



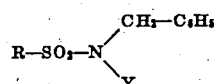
where R is an aryl radical other than a hydroxy substituted aryl radical, X is selected from the class consisting of alkyl and phenyl substituted alkyl radicals and Z is a naphthol residue, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic photographic developers.

5. In the method of producing a colored photographic image in a gelatino silver halide emulsion layer, the step which comprises treating the exposed layer containing a coupler compound having the formula:



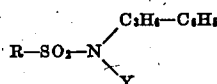
where R is an aryl radical other than a hydroxy substituted aryl radical, X is a phenyl substituted alkyl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developers with a developer containing a primary aromatic amino developing agent.

6. In the method of producing a colored photographic image in a gelatino silver halide emulsion layer, the step which comprises treating the exposed layer containing a coupler compound having the formula:



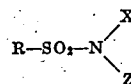
where R is an aryl radical other than a hydroxy substituted aryl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developers, with a developing solution containing a primary aromatic amino developing agent.

7. In the method of producing a colored photographic image in a gelatino silver halide emulsion layer, the step which comprises treating the exposed layer containing a coupler compound having the formula:



where R is an aryl radical other than a hydroxy substituted aryl radical and Y is selected from the class consisting of alkyl and aryl radicals, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developers, with a developing solution containing a primary aromatic amino developing agent.

8. In the method of producing a colored photographic image in a gelatino silver halide emulsion layer, the step which comprises treating the exposed layer containing a coupler compound having the formula:



where R is an aryl radical other than a hydroxy substituted aryl radical, X is selected from the class consisting of alkyl and phenyl substituted alkyl radicals and Z is a naphthol residue, said coupler compound containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developers, with a developing solution containing a primary aromatic amino developing agent.

ARNOLD WEISSBERGER.