

UNITED STATES PATENT OFFICE

2,289,804

SULPHONIC ESTER COUPLER

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This invention relates to color-forming development and particularly to novel coupling components for producing colored images.

It is known that colored photographic images may be formed by using a developer which forms a colored compound on development. The colored compound thus formed is deposited adjacent to the silver grains of the silver image during the development. It is also known that a colored image may be formed by adding to certain developer solutions or by incorporating in the gelatino-silver-halide emulsion before or after exposure a compound which couples during development with the oxidation product of the developing agent and forms a coloring substance which is likewise deposited adjacent to the silver grains of the silver image during development. Such a compound, which is employed in conjunction with a developing agent for the silver and which couples with the oxidation product thereof during development, is referred to herein as a coupling component or coupler.

The present invention concerns new or improved color forming developers comprising a primary aromatic amino compound serving as the developing agent, and a coupler as hereinafter defined and also includes a new or improved color development process which consists in developing a reducible silver salt image in a photographic element with the aid of a primary aromatic amino compound in the presence of a coupler as hereinafter defined. It also includes photographic sensitive elements having such a coupler incorporated in one or more emulsion layers.

In British Patent 503,752 sulphonic ester couplers are described which are obtained by the reaction of α -naphthol sulphonic acid chloride with phenols having a high molecular substituted amino or hydroxy group. In these couplers the hydroxyl group of the naphthol constitutes the coupling function and the sulphur atom of the sulphonic ester group is directly attached to the coupler portion of the molecule. While these compounds form colored photographic images upon development in primary aromatic amino developers, the coupler molecule in certain cases is unstable and is unsatisfactory for that reason.

I have found that sulphonic ester couplers in which the sulphur atom of the sulphonic ester group is not directly attached to a portion of the molecule containing a coupling function, that is, a reactive methylene or phenolic hydroxyl group are relatively stable compounds and con-

stitute desirable couplers. The couplers containing the sulphonic ester group are generally rendered less soluble by the incorporation of this group and are, therefore, satisfactory for the preparation of couplers for incorporation in photographic emulsions. They are, however, sufficiently soluble for use in developing solutions. The introduction of the sulphonic ester group tends to confer better dispersability on the coupler molecule, which is a desirable property when the coupler is to be incorporated in emulsions.

The compounds which I propose to use have the following general formula:

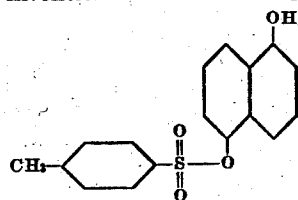


wherein

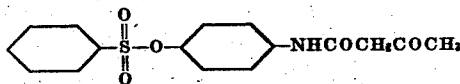
R=aryl or alkyl but does not contain a coupling function,

R'=an organic radical containing a coupling function, that is a reactive methylene or phenolic hydroxyl group.

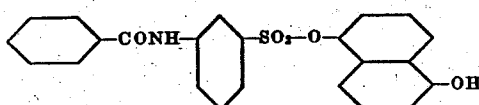
Specific compounds which may be used according to my invention are the following:



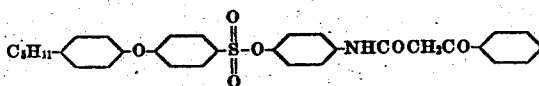
1-hydroxy-5-naphthyl-p-toluene sulphonate



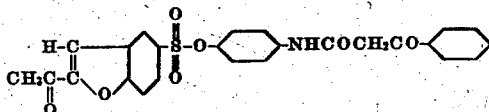
p-acetoacetaminophenyl benzene sulphonate



3-(benzoylamino)-1-(1-hydroxy-5-naphthyl)-benzene sulphonate



p-benzoylacetamino phenyl-4'-amyl-phenoxy-4-benzene sulphonate



2-acetyl-5-(4-benzoylacetaminophenyl-1)-coumaronyl sulphonate

These compounds can be prepared from intermediates not containing a coupling function and the coupling function then introduced as the final step. For example, p-acetoacetaminophenyl-benzene-sulphonate may be prepared in the following manner. Benzene sulphonyl chloride is reacted with p-nitrophenol to produce p-nitrophenylbenzenesulphonate. The nitro group is then reduced to an amine and is heated with ethylacetoacetate to introduce the coupling function and cause the formation of the sulphonic ester coupler.

The couplers made according to my invention may be dissolved in the developing solution or may be incorporated in the emulsion layer according to their solubility characteristics. The compounds indicated by the first two examples are suitable for use in the developing solution and those of the last two examples may be incorporated in the emulsion layer.

As stated above, the coupler must contain a coupling function but this coupling function may not be attached to the sulphur atom of the sulphonic ester group. By "coupling function" I mean a functional or reactive group common to coupler compounds which react with primary aromatic amino developing agents. This reactive group takes the form of a reactive methylene or reactive ethanol group. By "reactive methylene" I mean a CH_2 group which is reactive in the coupling process. The CH_2 group is usually present between two negative centers as in the groups



or



or in a ring system. Such examples of ring systems are oxindole and pyrazolone. One of the hydrogen atoms of the methylene group may, in general, be substituted by a polar group without destroying the chemical activity of the group. By "reactive ethanol" I mean the group



This group occurs in the phenolic and naphtholic coupler compounds which are presumably active in the o- or p- position with respect to the position of the hydroxyl group.

The coupling compounds used according to my invention may contain other substituents which do not affect the coupling properties of the compound. Where I refer in general formula to aryl and alkyl groups, it is to be understood that these groups may be further substituted provided that the other requirements with respect to coupling are met.

The aromatic amino developing agents used with the coupler compounds of my invention include the mono-, di- and tri-aminoaryl compounds and their derivatives formed by substitution in the amino group as well as in the ring, such as alkylphenylenediamines and alkyl-toluylenediamines. These compounds are usually used in the salt form, such as the hydrochloride or the sulphate, which are more stable than the amines themselves. Suitable compounds are diethyl-p-phenylenediamine hydrochloride, monoethyl-p-phenylenediamine hydrochloride, dimethyl-p-phenylenediamine hydrochloride and dimethyl-p-phenylenediamine sulphate. Developing agents containing heterocyclic systems as described in U. S. Patent 2,196,739 are also suitable. The p-aminophenols

and their substitution products may also be used where the amino group is unsubstituted. All of these compounds have an unsubstituted amino group which enables the oxidation products of the developer to couple with the color-forming compounds to form a dye image.

The following developer formulas may be used with the compounds of my invention:

A.	p-Aminodiethylaniline sulphate	grams	2
	Sodium sulphite anhydrous	do	5
	Sodium carbonate anhydrous	do	20
	Potassium bromide	do	2
	Water to	liter	1
B.	Coupler	grams	1 to 5
	Isopropyl alcohol	cc	100

B is added to A

My development process may be employed for the production of colored photographic images in layers of gelatin or other carrier such as collodion, organic esters of cellulose or synthetic resins. The carrier may be supported by a transparent medium such as glass, a cellulose ester, or a non-transparent reflecting medium such as paper of an opaque cellulose ester. The emulsion may be coated as a single layer on the support or as superposed layers on one or both sides of the support. The superposed layers may be differentially sensitized to form natural color photographic images in the well known manner.

The examples and compounds set forth in the present specification are illustrative only and it is to be understood that my invention is limited only by the scope of the appended claims.

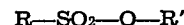
I claim:

1. A color forming photographic developer, comprising a primary aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developing agents.

2. A color forming photographic developer, comprising a primary aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical comprising a reactive ethenol coupling function.

3. A color forming photographic developer, comprising a primary aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical comprising a reactive ethenol coupling function.

4. A color forming photographic developer, comprising a primary aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of

alkyl and aryl radicals not containing a coupling function and R' is a naphthol.

5. A color forming photographic developer, comprising a primary aromatic amino developing agent and a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical comprising an acetamino group.

6. A color forming photographic developer comprising a primary aromatic amino developing agent and 1-hydroxy-5-naphthyl-p-toluene-sulphonate as a coupling compound.

7. A color forming photographic developer comprising a primary aromatic amino developing agent and p-acetoacetamino phenylbenzene-sulphonate as a coupling compound.

8. The method of producing a colored photographic image in a gelatino-silver halide emulsion layer which comprises exposing the layer and developing it with a primary aromatic amino developing agent in the presence of a coupler compound having the formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical contain-

ing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developing agents.

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



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developing agents.

10. A photographic emulsion for forming colored images comprising a gelatino-silver halide emulsion having incorporated therein a coupler compound of the general formula:



where R is selected from the class consisting of alkyl and aryl radicals not containing a coupling function and R' is an organic radical containing at least one group selected from the class consisting of methylene and ethenol which is reactive with primary aromatic amino developing agents.

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