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COLOR FORMING COMPOUNDS CONTAINING SULPHONAMIDE GROUPS

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7 Claims. (Cl. 95—6)

This invention relates to photographic color forming compounds and particularly to color forming coupler compounds containing sulphonamide groups.

This application is a continuation-in-part of our application Serial No. 266,152, filed April 5, 1939, now Patent 2,271,238, granted January 27, 1942.

The use of color forming compounds which react with the development product of primary aromatic amino developing agents to form color images on photographic development is well known and has 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. The coupler compounds used in this way may be added to the developing solution or in certain cases may be incorporated in the photographic layer prior to exposure. When the coupler compounds are incorporated in the developing solution, it is desirable that they be sufficiently soluble in the developing solution so that amounts may be used which produce sufficiently high dye densities in the resulting photographic image. In many cases the coupler compounds are not sufficiently soluble in the developer and steps must be taken to increase their solubility.

In Schinzel application Serial No. 263,945, filed March 24, 1939, a continuation-in-part of Serial No. 151,811, filed July 3, 1937, now Patent 2,306,410, granted December 29, 1942, phenolic and naphtholic coupler compounds are described which contain sulphonamide groups in which the sulphur of the sulphonamide is attached to the phenol or naphthol. These compounds are highly soluble in the developing solutions and produce dyes which are transparent and are not cloudy or opaque as is the case with many dyes produced in this way. These dyes are, however, subject to decomposition by the action of heat and light and it is, therefore, desirable to produce dyes having the solubility and light transmission characteristics of the dyes described in the Schinzel application but which are more stable to heat and light.

It is, therefore, an object of the present invention to provide novel photographic coupler compounds having desirable properties with respect to heat and light stability. A further object is to provide photographic couplers which are highly soluble in developing solutions. A still further object is to provide photographic couplers which produce transparent dyes on photographic development. A still further object is to provide coupler compounds which produce dyes of desirable light transmission characteristics for multicolor photography. Other objects will appear from the following description of our invention.

These objects are accomplished by the use of certain coupler compounds containing sulphonamide groups.

The color-forming compounds which we have found to be useful are compounds of the general structure

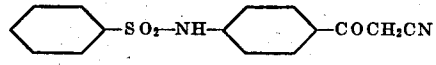
$$R—SO_2NH—R'$$

or

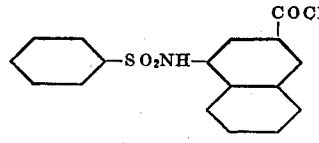
$$R—NHSO_2—R'$$

in which R represents a substituted or unsubstituted aryl radical or alkyl radical and R' represents a cyanoacetylaryl group, such as a cyanoacetylphenyl or cyanoacetylnaphthyl group, or a cyanoacetanilide group.

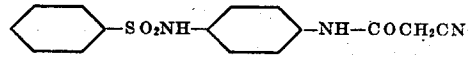
Compounds suitable for use according to our invention are as follows:



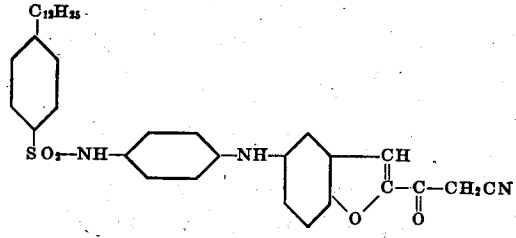
p-(benzenesulphonamino)-benzoyl acetonitrile



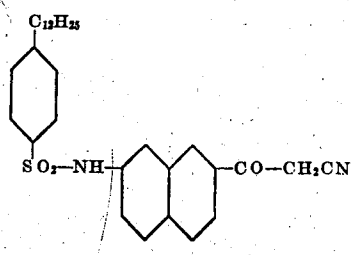
4-(benzenesulphonamino)-2-naphthoyl-acetonitrile



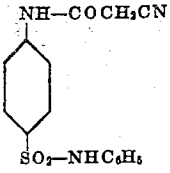
p-benzenesulphonamino-cyanoacetanilide



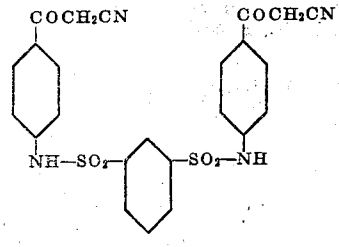
2-cyanoacetyl-5-[p(p-lauryl benzene sulphonamino)phenylamino]-coumarone



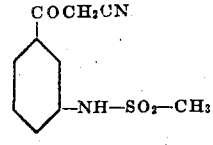
2-cyanoacetyl-7-(p-laurylbenzenesulphonamino)-naphthalene



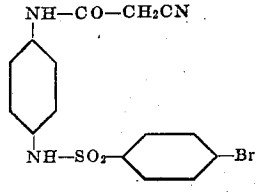
p-(cyanoacetamino)-benzenesulphonanilide



N,N'-di-(p-cyanoacetylphenyl)-benzene-1,3-disulphonamide



m-(methanesulphonamino)-benzoylacetonitrile



p-(4-bromobenzenesulphonamino)-cyanoacetanilide

The coupler compounds having the general formula:

$$R—SO_2NH—R'$$

or

$$R—NHSO_2—R'$$

contain a methylene group which is reactive with the oxidation product of primary aromatic amino photographic developers to produce magenta dyes.

The following example, which is illustrative only, is a developing solution containing a coupler suitable for use according to our invention.

A. p-Aminodimethylanilinesulphate	grams	2.5
Sodium sulphite (anhydrous)	do	2
Sodium carbonate (anhydrous)	do	20
Potassium bromide	do	1
Water to	cc	1000
B. p-Benzenesulphonaminocyanoacetanilide	grams	2
Sodium hydroxide—10% solution	cc	10

B is added to A

In the foregoing example, we have described adding the coupler compound to the developing solution itself. Although it will usually be employed in this way, the coupler compound may also be incorporated in the photographic layer prior to exposure and the colored image formed by development of the layer in the primary aromatic amino developing solution. Special dispersing agents may be used for incorporating the coupler compound in the emulsion and in certain cases the coupler may be absorbed or adsorbed to the sensitive salt or may be combined with the sensitive salt as a chemical combination.

In the case of a multi-layer photographic film in which color forming compounds may be incorporated in one or more of the layers, it may be necessary to take special precautions to prevent wandering of the coupler compound from the sensitive layer in which it is incorporated. Certain of the coupler compounds described in the present application are in themselves non-diffusing and may be incorporated in the photographic layer without the use of additional agents to prevent diffusion. The compound 2-cyano-acetyl-7-(p-laurylbenzenesulphonamino) - naphthalene is an example of this type coupler.

The sulphonamide group, because of its solubilizing effect, has a very important advantage in connection with non-diffusing couplers in that it makes dispersion of the couplers very much easier. Thus it is possible to have a coupler of high molecular weight which is completely non-diffusing and yet which is simply and easily dispersed due to the salt-forming properties of the —SO_2—NH— group.

The aromatic amino developing agents used with the coupler compounds of our 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 alkyltoluylenediamines. 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, monomethyl - p - phenylenediaminehydrochloride, dimethyl-p-phenylenediaminehydrochloride and dimethyl-p-phenylenediaminesulphate. 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.

Our 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 or 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 and the dyes formed therein by coupling may be bleached by an oxidizing agent such as chromic acid to colorless soluble compounds. The destruction of the dye in this way does not destroy the silver image and a silver image may be developed, bleached and developed to color a number of times, thus permitting the formation of natural color images in superposed layers as described, for example, in Mannes and Godowsky U. S. Patent No. 2,113,329.

The examples and compounds set forth in the present specification are illustrative only and it is to be understood that our invention is to be taken as limited only by the scope of the appended claims. Where we describe organic groups such as aryl, arylene, alkyl, and sulphonamide in the specification and claims, we intend to include the substituted, as well as unsubstituted, groups, except where certain groups are specifically excluded.

We claim:

1. A color-forming photographic developer comprising a primary aromatic amino developing agent and a coupler compound having a formula selected from the group consisting of

$$R—SO_2NH—R'$$

or

$$R—NHSO_2—R'$$

where R is selected from the group consisting of alkyl and aryl radicals and R' is a cyanoacetyl-aryl group.

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

$$R—SO_2NH—R'—COCH_2CN$$

where R is an aryl radical and R' is an arylene radical.

3. A color-forming photographic developer comprising a primary aromatic amino developing agent and p(benzenesulphonamino)-benzoyl acetonitrile.

4. A color-forming photographic developer comprising a primary aromatic amino developing agent and 4-(benzenesulphonamino)-2-naphthoyl acetonitrile.

5. 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 a formula selected from the group consisting of

$$R—SO_2NH—R'$$

and

$$R—NHSO_2—R'$$

where R is selected from the group consisting of alkyl and aryl radicals and R' is a cyanoacetyl-aryl group.

6. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and a coupler compound having a formula selected from the group consisting of

$$R—SO_2NH—R'$$

and

$$R—NHSO_2—R'$$

where R is selected from the group consisting of alkyl and aryl radicals and R' is a cyanoacetyl-aryl group.

7. A photographic emulsion for forming colored images comprising a colloidal carrier containing a sensitive silver halide and 2-cyanoacetyl-7-(p-laurylbenzenesulphonamino)-naphthalene as a coupler.

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