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2,271,230

SULPHONAMIDES OF DYES

Filed Aug. 31, 1940

FIG. 1

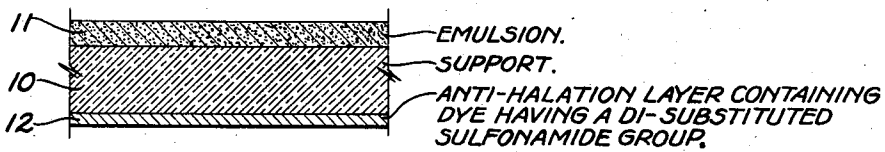
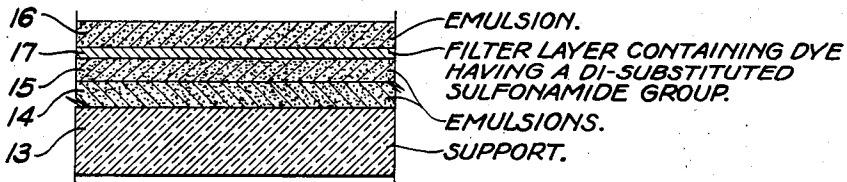


FIG. 2



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## UNITED STATES PATENT OFFICE

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## SULPHONAMIDES OF DYES

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Company, Rochester, N. Y., a corporation of  
New Jersey

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In Great Britain September 7, 1939

6 Claims. (Cl. 95—2)

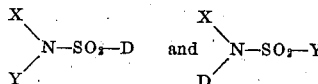
This invention relates to sensitive photographic materials having coloring matters therein.

Coloring matters are required in sensitive photographic materials for many purposes. Thus, it is often necessary to incorporate in photographic emulsions coloring matters to act as filters or to serve for the production of colored images by differential bleaching in the image and non-image areas. Coloring matters may be introduced into emulsion layers or into grains of silver halide emulsion disposed in a carrier, or into the carrier for such grains, especially in the case of elements for color photography having two or more layers or sets of grains on one or more supports. Furthermore, coloring matters may be present in layers other than those containing the sensitive silver halide, e. g. in filter layers over or under sensitive emulsion layers or between two sensitive emulsion layers or in backing serving, for example, as anti-halation layers. In many cases it is desirable to use for these purposes coloring matters which will not diffuse during coating nor during the processing of the materials. Since, in the processing, acid or alkaline baths may be used it may be necessary to use coloring matters which are resistant to either acid or alkali or both. Numerous coloring matters for these purposes have been proposed in the past, but it is always a matter of difficulty to avoid their diffusion from the place where they are required to be present.

Another disadvantage is also sometimes encountered. If the coloring matter is one which contains free aromatic amino or hydroxyl groups, it may give rise to stains when the element containing it is subjected to the action of a color developer, due presumably to the formation of an indophenol or indamine.

We have now found that suitable coloring matters to employ in photographic elements for any of the purposes indicated are those containing a sulphonylamide group, especially those in which both hydrogen atoms on the amido nitrogen atom are substituted by organic radicals. Such color-

ing matters are represented by either of the formulae.



where

D=a dye portion, that is, the residue of a coloring matter,

X and Y=alkyl or aryl, which may be substituted or unsubstituted

If an N-substituted sulphonamide group is introduced into a dyestuff, there is in many cases a desirable change in the color. At the same time the solubility and dispersibility of the dye in gelatin or other carrier is greatly increased without appreciably altering the acidity or basicity of the original dye.

In the accompanying drawing

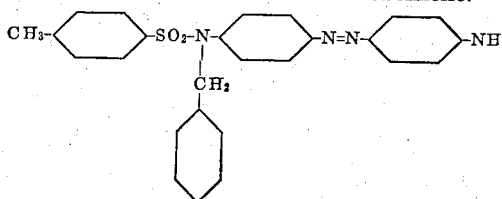
Fig. 1 is a sectional view of a photographic element made according to one modification of our invention, and

Fig. 2 is a sectional view of a photographic element made according to another modification of our invention.

The following examples, which are illustration only, indicate compounds which may be used in photographic layers according to our invention:

## Example 1

The compound N-(p-tolyl-sulphonyl)-N-(benzyl)-4-amino-azobenzene, whose structure is as follows, is a purer yellow (minus blue) and is more easily dispersed in gelatin than the corresponding unsubstituted 4-aminoazobenzene.

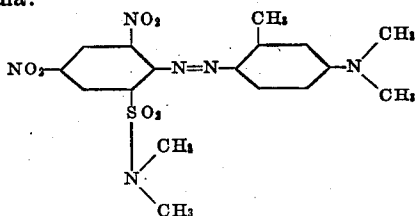


This compound is not affected by acid processing

solutions. It may be used as a yellow dye in a bleach-out process using acid bleaching baths for differential bleaching in the image or non-image areas.

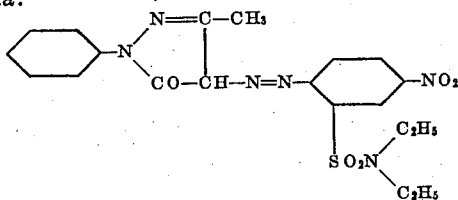
#### Example 2

The compound 2,4-dinitro-6 (sulphondimethylamide)-benzeneazo-1'-methyl-4'-dimethylamino benzene is a magenta dye having the following formula:



#### Example 3

The compound 1-phenyl-3-methyl-4(4'-nitro-6-sulphonedietethylamide-benzeneazo)-5-pyrazolone is a yellow dye which can be used in a filter or anti-halation layer. It has the following formula:



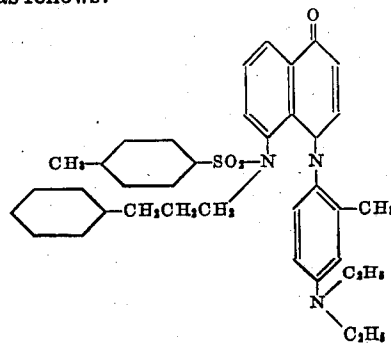
#### Example 4

Dyes according to our invention may also be made by generating an azomethine or indophenol dye containing a sulphonamide group in the gelatin itself. This example illustrates a method of developing a dye of the indophenol type in gelatin by the use of a coupler which can be easily dispersed in gelatin by virtue of a di-substituted sulphonamide group in its molecule.

Three and three-tenths grams of 5-[N,N(γ-phenylpropyl)-(p-tolyl)sulphonamidol]-1-naphthol is dissolved in 60 cc. of ethyl alcohol and 5 cc. of 20 per cent sodium hydroxide. This solution is added to one liter of a 10 per cent photographic gelatin solution. To this solution is added 1.5 grams of 2-amino-5-diethylaminotoluene hydrochloride which has been dissolved in 10 cc. of water. With good stirring, the calculated amount of an oxidizing agent, such as a 10 per cent solution of potassium ferricyanide, is added slowly, whereupon a brilliant cyan dye is generated uniformly throughout the gelatin. This

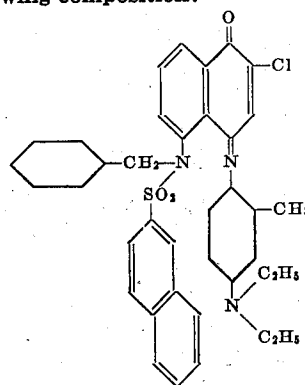
colored gelatin is adjusted to the desired pH and washed thoroughly with cold water. Such a dyed gelatin solution may be used as an antihalation or filter layer, or it may be mixed with silver halide emulsion and used in a light-sensitive lay-

er. The structural formula of the resulting cyan dye is as follows:



#### Example 5

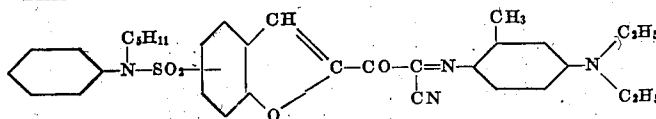
In a similar manner an indophenol dye may be formed from 2-chloro-5-(β-naphthalenesulphonbenzylamido)-1-naphthol and 2-amino-5-diethylaminotoluene hydrochloride forming a dye of the following composition:



This method of generating dyes in gelatin can be extended to the production of dyes of the azo and azomethine types by starting with couplers having sulphonamide groups which permit their uniform dispersion in gelatin. These gelatin-coupler solutions are treated either with the diazonium salt solutions in order to generate azo dyes or with p-phenylenediamine compounds containing a free amino group with a mild oxidizing agent to generate azomethine dyes. The advantage of this method lies in the fact that the dye itself would be dispersed with difficulty whereas the coupler of smaller molecular weight can be readily dispersed uniformly in the gelatin.

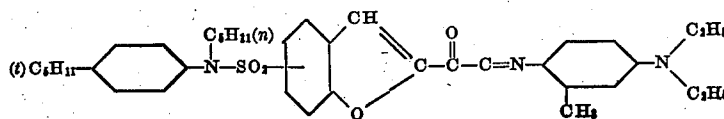
#### Example 6

An azomethine dye is made from cyanoacetyl-coumarone-sulphon-N-amplanilide and 2-amino-5-diethylaminotoluene hydrochloride, having the following composition:



#### Example 7

An azomethine dye is made from cyanoacetyl-coumarone-χ-sulphon-N-n-amylyl-p-tertiary amyl anilide and 2-amino-5-diethylaminotoluene hydrochloride, having the following composition:



## Example 8

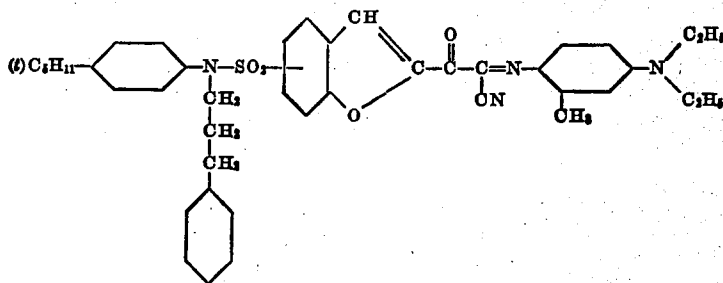
An azomethine dye is made from cyanoacetyl-coumarone- $\chi$ -sulphon-N-( $\chi$ -phenylpropyl)-p-tertiary-amyranilide and 2-amino-5-diethylaminotoluene hydrochloride, having the following formula:

where

D=a dye portion

X and Y=alkyl, aryl.

2. A light-sensitive photographic element including a filter layer comprising gelatin having therein a non-diffusing dye having attached



In the production of dyes from couplers according to this method, sulphonamide couplers are used which may be considered as having been derived from a secondary amine, that is, the sulphonamide group is substituted with alkyl or aryl radicals. Couplers of this type are described in Weissberger U. S. application Ser. No. 253,669, filed August 22, 1940.

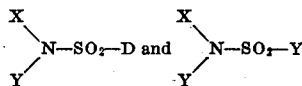
Our invention will now be described with reference to the accompanying drawing. As shown in Fig. 1 thereof, 10 is a support of any suitable transparent material such as glass, cellulose ester or synthetic resin having thereon a sensitive emulsion layer 11. On the opposite side of the support 10 there is coated a gelatin layer 12 containing a dye having a di-substituted sulphonamide group made according to our invention. Fig. 2 illustrates a multi-layer element having a support 13 of transparent material such as glass, cellulose ester or synthetic resin or opaque material such as paper or opaque cellulose ester. On the support 13 are coated emulsion layers 14, 15 and 16 sensitive, respectively, to different regions of the visible spectrum. Between emulsion layers 15 and 16 there is a gelatin layer 17 containing a yellow filter dye containing a di-substituted sulphonamide group according to our invention.

The quantity of dye used in the filter and anti-halation layers made according to our invention may vary according to the tinctorial strength of the dye and the optical density desired. An average quantity of dye is about 2-5 grams per liter of 10% gelatin solution.

The examples and quantities included in the above 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.

We claim:

1. A light-sensitive photographic element including a filter layer comprising gelatin having therein a non-diffusing dye having a general formula selected from the class consisting of

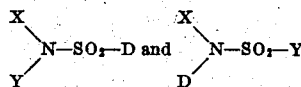


20 thereto a sulphonamide group in which both free hydrogen atoms are replaced with aryl nuclei.

3. A photographic element comprising a support having thereon three emulsion layers sensitive respectively to the red, green, and blue regions of the spectrum, and between the blue-sensitive and the green-sensitive layers, a gelatin filter layer containing a 4-amino-azobenzene in which one of the hydrogen atoms of the amino group is replaced with an aromatic sulphonyl group and the other hydrogen atom is replaced with a substituted alkyl group.

4. A photographic element comprising a support having thereon three emulsion layers sensitive respectively to the red, green, and blue regions of the spectrum, and between the blue-sensitive and the green-sensitive layers, a gelatin filter layer containing a 4-amino-azobenzene in which one of the hydrogen atoms of the amino group is replaced with an aromatic sulphonyl group and the other hydrogen atom is replaced with a benzyl group.

5. A light-sensitive photographic element including a layer comprising gelatin having therein a non-diffusing dye having a general formula selected from the class consisting of



where

D=a dye portion selected from the group consisting of azo, azomethine and indo-phenol dyes

X and Y=alkyl, aryl.

6. The method of making a photographic filter layer which comprises mixing with a gelatin solution a primary aromatic amino developing agent and a sulphonamide coupler derived from a secondary amine and containing a group reactive with the oxidation product of said developing agent, mixing an oxidizing agent with said gelatin solution to oxidize said developing agent and produce a dye with said sulphonamide coupler, and coating the dye-containing gelatin solution on a photographic support.

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