

## UNITED STATES PATENT OFFICE

2,286,838

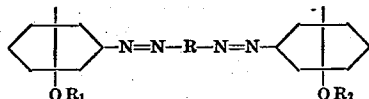
PHOTOGRAPHIC ELEMENT CONTAINING A  
DISAZO DYE

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14 Claims. (Cl. 95-6)

This invention relates to a photographic element and more particularly to a single or multi-layer photographic element wherein at least one of the layers is uniformly colored with a dye selected from the group of disazo compounds having the general formula:



wherein R represents a member selected from the group consisting of a naphthalene disulfonic acid nucleus, a dibenzyl disulfonic acid nucleus, a diphenyl disulfonic acid nucleus, a di-tolyl disulfonic acid nucleus, a stilbene disulfonic acid nucleus, and a diphenyl urea disulfonic acid nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a saturated alkyl group having a chain length of at least 3 carbon atoms and not greater than 5 carbon atoms. The nuclei of R can be further substituted by one or more monovalent substituents selected from the group including methyl, ethyl, propyl, butyl, methoxy, ethoxy, propoxy, methoxymethyl, methoxyethyl, chlorine, bromine, and the like groups.

It is well known in the photographic art that dyes used in photographic layers such as filter dyes, antihalation dyes and image-forming dyes should remain fixed in the layers wherein they are incorporated. Many of the dyes proposed tend to migrate from one layer to another, while others are sufficiently non-diffusible, but have the disadvantage of being difficult to incorporate because of limited solubility characteristics, or, if capable of ready incorporation, cannot be satisfactorily bleached or removed from the layers during the processing. It has also been proposed that by merely increasing the molecular size of certain dye molecules such as by introducing long-chain aliphatic substituents into the dye nuclei that desirable non-diffusing products can be obtained.

While it is in general true that increase in molecular size of the dye molecule tends to limit its mobility, we have found, however, that a desirable dye for photographic layers depends not only on the type of dye and upon the molecular size, but also upon the chain-length of the specific substituents. Thus, we have found that the above described disazo compounds of our invention are highly desirable coloring materials for photographic layers with none of the disadvantages mentioned. They do not seriously desensitize the emulsions in which they are in-

corporated, and may be readily decolorized by suitable treatment of the film. The fact that the chain length of the alkyl groups R<sub>1</sub> and R<sub>2</sub> is critical can be shown by the fact that chrysophenine G, wherein R<sub>1</sub> and R<sub>2</sub> are ethyl groups, diffuses very badly from one photographic gelatin layer to another, whereas the various corresponding propyl, butyl and amyl substituents are completely or almost completely non-diffusing. While the corresponding higher alkyl members, that is, those of greater than 5 carbon atom chain lengths are likewise non-diffusing, we have found them unsuitable, because of difficulty of incorporating them into the compositions from which our photographic layers are formed, and because of difficulty of bleaching these dyes to form photographic images. Moreover, the dyes with more than 5 carbon atoms in the alkyl chains are more expensive to manufacture.

It is an object of our invention, therefore, to provide photographic layers having disazo dyes contained therein which do not diffuse through set gelatin or which diffuse only slightly. A further object is to provide dyes which do not seriously desensitize emulsion layers in which they are incorporated and do not desensitize emulsions which are coated adjacent to the dye-containing layers. A still further object is to provide dyes for color photography which can be bleached readily in the presence of a silver image by the use of a suitable bleaching agent. Another object is to provide image-forming dyes for color photography which have the proper spectral absorption ranges. Other objects will appear from the following description of our invention.

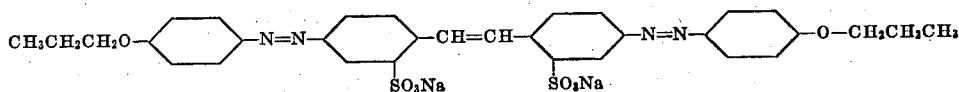
These objects are accomplished by the use of the above described disazo dyes which can be prepared by tetrazotizing symmetrical aromatic diamines such as 4,4'-diamino-stilbene-2,2'-disulfonic acid, benzidine-3,3'-disulfonic acid, tolidine disulfonic acids, 1,5-diamino-naphthalene disulfonic acids, 4,4'-diamino-dibenzyl disulfonic acid, 4,4'-diamino-3,3'-disulfo-diphenyl urea, and the like, and coupling with 2 moles of phenol or its substitution products and converting to the propyl, butyl or amyl ethers by known means.

The following examples, which are illustrative only, indicate dyes which are suitable for use according to our invention.

*Example 1*

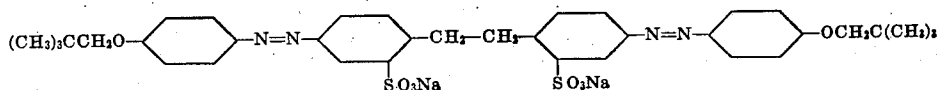
The dye made by tetrazotizing 1 mole of 4,4'-diamino-stilbene-2,2'-disulfonic acid and cou-

pling it in an alkaline medium with 2 moles of phenol and then converting to the n-propyl ether having the following structure:



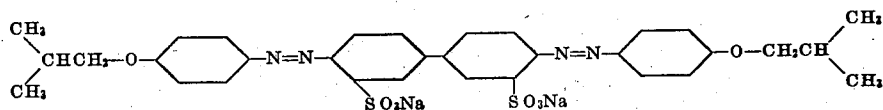
In place of the normal propyl ether, there can be employed the corresponding isopropyl, butyl and amyl ethers.

**Example 5**  
The dye made by tetrazotizing 1 mole of a 4,4'-diamino-dibenzyl-disulfonic acid and coupling in

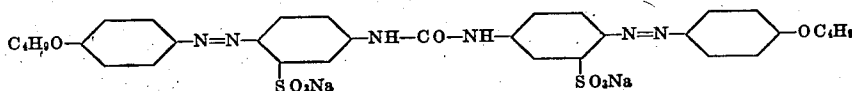


#### Example 2

The dye made by tetrazotizing 1 mole of benzi-dine-3,3'-disulfonic acid and coupling it in an alkaline medium with 2 moles of phenal and then converting to the isobutyl ether having the following structure:

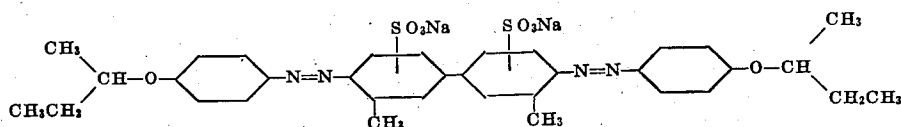


having the following structure:

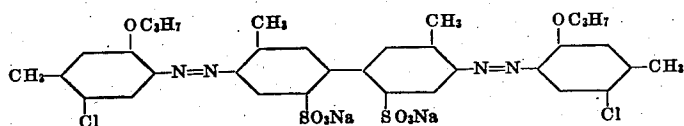


#### Example 3

The dye made by tetrazotizing 1 mole of toli-dine disulfonic acid and coupling in an alkaline medium with 2 moles of phenol and then converting to the sec-butyl ether having the following structure:

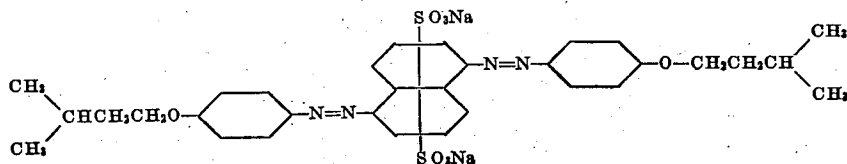


having the following structure:



#### Example 4

The dye made by tetrazotizing 1 mole of 1,5-di-amino-naphthalene disulfonic acid and coupling in an alkaline medium with 2 moles of phenol and converting to the primary-isoamyl ether having the following structure:



**Example 6**  
The dye made by tetrazotizing 1 mole of 4,4'-diamino-diphenyl urea-3,3'-disulfonic acid and coupling in an alkaline medium with 2 moles of phenol, and then converting to the n-butyl ether

#### Example 7

The dye made by tetrazotizing 1 mole of o-toli-dine disulfonic acid and coupling in an alkaline medium with 2 moles of 2-chloro-5-hydroxy toluene, and then converting to the n-propyl ether

layer of dye in the vicinity of a silver image by special treatment with solutions containing thiourea or hydrobromic acid and a catalyst, or, with a solution of sodium stannite as described in copending application Serial No. 360,622 filed October 10, 1940.

When used as image-forming dyes in light sensitive photographic layers, the dyes which we have described may be used in a photographic material such as that described in Christensen U. S. Patent No. 1,517,049, issued November 5, 1924. In the material described in the Christensen patent, the sensitive layers are uniformly colored a color complementary to that which they are designed to record. The blue-sensitive layer is colored yellow, the green-sensitive layer is colored magenta and the red-sensitive layer is colored blue-green. However, the dyes used according to our invention may also be incorporated in layers which are sensitive to any color. For example, the dyes proposed according to our invention, all of which are yellow, may be incorporated in a green-sensitive layer or a red-sensitive layer as well as in a blue-sensitive layer of a multi-layer coating.

The sensitive compositions containing our dyes may be coated on transparent film supports such as a derivative of cellulose including cellulose nitrate, cellulose acetate, cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-butyrate, cellulose ether, and the like, as well as on a synthetic resin support such as a polyvinyl acetal, and opaque supports such as paper or cellulose derivatives mixed with opaque white pigments. They may be used in single layer or multi-layer coatings or in multi-layer coatings on one or both sides of a support.

In certain cases the dyes we propose to use may be bleached in suitable alkaline bleaching solutions such as sodium stannite. The dye may be bleached in the presence of a silver salt image which is converted to a silver image in the same operation.

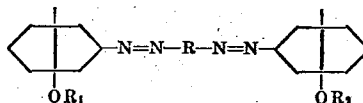
Dyes of the structure which we have described are practically non-diffusing in gelatin, and have little or no adverse effect on the sensitivity of the emulsion in which they are incorporated or on adjacent emulsion layers. They may be bleached in the presence of a silver or silver salt image as stated above and when used in filter layers, they may be discharged by the use of sodium hydrosulfite or potassium permanganate and acid.

Furthermore, the dyes which we have proposed have good water solubility, thus facilitating the preparation of dyed layers of adequate dye density without crystallization of the dye. Although our dyes may contain various monovalent substituents, it should be noted that the solubilizing groups are limited in number to avoid too great a tendency to diffuse. For example, some non-diffusible dyes can be made to diffuse by introducing an excessive number of sulfonic acid groups into the dye molecule. This fact is well known in the dye art and we do not intend to include within the scope of our invention dyes containing an excess number of solubilizing groups which increase the diffusion tendency. In general, dyes of the types described in our invention are satisfactory with two sulfonic acid groups in the molecule, but may diffuse with a greater number of sulfonic groups.

We claim:

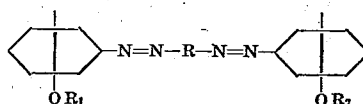
1. A photographic element comprising a sup-

port having thereon a light-sensitive layer, at least one layer comprising a water-permeable colloid and a dye having the general formula:



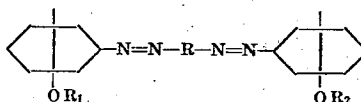
wherein R represents a member selected from the group consisting of a naphthyl nucleus, a dibenzyl nucleus, a diphenyl nucleus, a diphenylurea nucleus, and a stilbene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said nuclei contain two sulfonic acid groups as nuclear substituents.

2. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising a water-permeable colloid and a dye having the general formula:



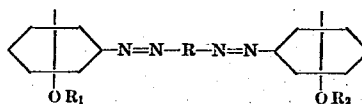
wherein R represents a stilbene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the stilbene nucleus contains two sulfonic acid groups as nuclear substituents.

3. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising a water-permeable colloid and a dye having the general formula:



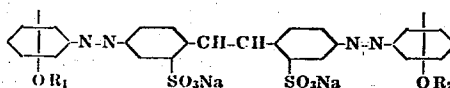
wherein R represents a diphenyl nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said diphenyl nucleus contains two sulfonic acid groups as nuclear substituents.

4. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising a water-permeable colloid and a dye having the general formula:



wherein R represents a naphthalene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said naphthalene nucleus contains two sulfonic acid groups as nuclear substituents.

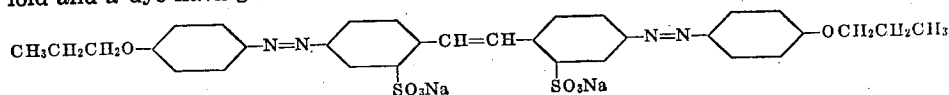
5. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising a water-permeable colloid and a dye having the general formula:



wherein R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms.

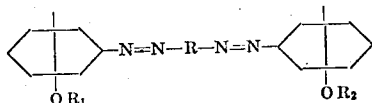
6. A photographic element comprising a support having thereon a light-sensitive layer, at

least one layer comprising a water-permeable colloid and a dye having the formula:



wherein R represents a naphthalene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected

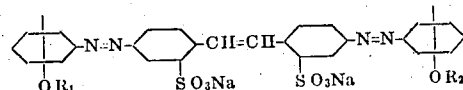
7. A gelatino-silver halide layer for a dye-bleaching process of color photography, uniformly colored with a dye having the general formula:



wherein R represents a member selected from the group consisting of a naphthyl nucleus, a dibenzyl nucleus, a diphenyl nucleus, a diphenylurea nucleus, and a stilbene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said nuclei contain two sulfonic acid groups as nuclear substituents.

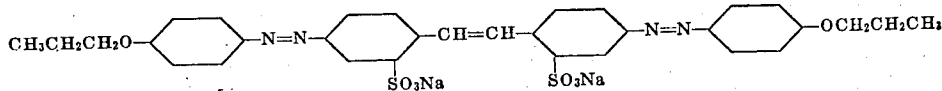
from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said naphthalene nucleus contains two sulfonic acid groups as nuclear substituents.

11. A gelatino-silver halide layer for a dye-bleaching process of color photography uniformly colored with a dye having the general formula:

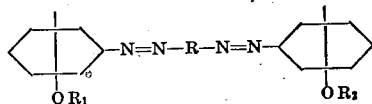


wherein R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms.

12. A gelatino-silver halide layer for dye-bleaching process of color photography uniformly colored with a dye having the formula:

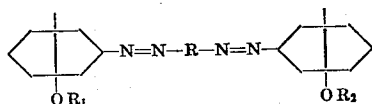


8. A gelatino-silver halide layer for a dye-bleaching process of color photography uniformly colored with a dye having the general formula:



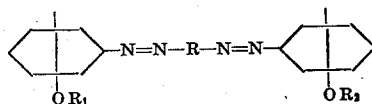
wherein R represents a stilbene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the stilbene nucleus contains two sulfonic acid groups as nuclear substituents.

9. A gelatino-silver halide layer for a dye-bleaching process of color photography uniformly colored with a dye having the general formula:

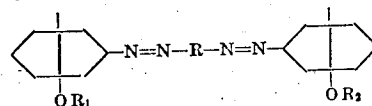


wherein R represents a diphenyl nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said diphenyl nucleus contains two sulfonic acid groups as nuclear substituents.

10. A gelatino-silver halide layer for a dye-bleaching process of color photography uniformly colored with a dye having the general formula:

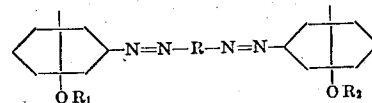


13. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising gelatin and a dye having the general formula:



wherein R represents a member selected from the group consisting of a naphthyl nucleus, a dibenzyl nucleus, a diphenyl nucleus, a diphenylurea nucleus, and a stilbene nucleus, and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the said nuclei contain two sulfonic acid groups as nuclear substituents.

14. A photographic element comprising a support having thereon a light-sensitive layer, at least one layer comprising gelatin and a dye having the general formula:



wherein R represents a stilbene nucleus and R<sub>1</sub> and R<sub>2</sub> each represents a member selected from the group consisting of saturated alkyl groups of from 3 to 5 carbon atoms, and wherein the stilbene nucleus contains two sulfonic acid groups as nuclear substituents.

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