

United States Patent

[11] 3,615,582

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|------|-----------|---|
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| [32] | Priority | Dec. 13, 1967 |
| [33] | | Germany |
| [31] | | P 15 97 504.9 |

- [50] **Field of Search**..... 96/99, 96,
73, 77; 117/34

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Assistant Examiner—Theodore G. Davis
Attorney—Connolly and Hutz

- [54] PHOTOGRAPHIC MATERIALS FOR THE SILVER
DYE BLEACH PROCESS
12 Claims, No Drawings**

- [52] U.S. Cl..... 96/99,
96/96, 96/77
[51] Int. Cl..... G03c 1/40

ABSTRACT: The provision in a light-sensitive silver-dye-bleach silver halide emulsion of a bis-azo dye which is a light fast yellow dye compatible with photographic layers to provide uniform distribution and having brilliant spectral properties by resisting side absorption.

PHOTOGRAPHIC MATERIALS FOR THE SILVER DYE BLEACH PROCESS

This invention relates to color photographic materials for the silver-dye-bleach process which materials contain particularly light-fast yellow azo dyes.

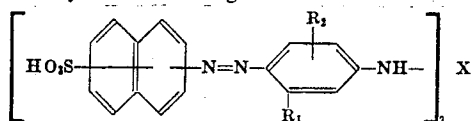
It is known that color photographic images can be produced by the silver-dye-bleach process, wherein a dye, usually an azo dye, is bleached in a homogeneously dyed colloid layer in accordance with a silver image which had been produced photographically.

It is possible to produce both negative and reversal silver-dye-bleach images. If it is desired to produce positive paper prints or duplicate positives from diapositives, the silver image is produced by means of a simple black-and-white development, this silver image representing a negative of the copying original. Since the image dye which is homogeneously distributed in the layer (or in the three layers of a multicolor material) is bleached proportionately to the silver image a dye image is obtained, which is positive with respect to the original. If a silver image is produced which is positive with respect to the original, for example, by a black-and-white reversal development or by the bromide ion diffusion method or silver salt diffusion method, then after the color bleaching a dye image is formed which is opposite in gradation to the original, that is to say a positive color image is formed if the original is a negative color image.

The standards set as regards dyes for the process described are particularly high, since these dyes must be spectrally suitable, and should also be easily bleachable and fast to light. Furthermore, they must be completely resistant to diffusion in the gelatin which is almost exclusively used as layer former. Excellent light fastness is of particular importance but resistance to acid gases such as occur in the atmosphere in industrial areas, and high brilliance, i.e. freedom from side absorption in undesired spectral regions combined with suitable spectral position of the absorption, are also of importance.

It is among the objects of the invention to provide yellow azo dyes which are easily to prepare, are compatible with the photographic layers, and have spectral properties which satisfy the various requirements of the silver-dye-bleach process.

The above objects have been attained by providing a yellow bis-diazo dye of the following formula:



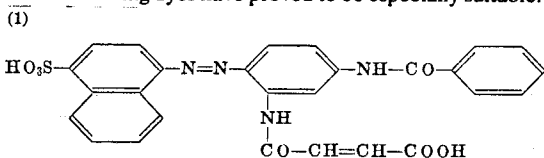
wherein

R_1 = (1) hydrogen, (2) an alkyl group with preferably up to three carbon atoms, (3) halogen such as chlorine or bromine, (4) an alkoxy group with preferably up to three carbon atoms, (5) an acylamino group in which the acyl groups are advantageously derived from aliphatic mono- or dicarboxylic acids which have up to six carbon atoms or from benzene carboxylic acids, especially benzoic acid, or (6) an ureido group;

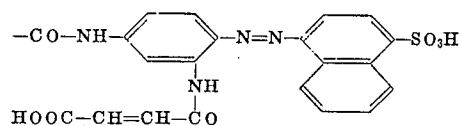
R_2 = hydrogen, an alkyl or alkoxy group having preferably up to three carbon atoms or halogen such as chlorine or bromine;

X = (1) carbonyl, (2) an acyl group derived from a saturated or olefinically unsaturated aliphatic dicarboxylic acid having preferably up to 12 carbon atoms, such as $-\text{COCH}_2\text{CHCO}-$, $-\text{CO}(\text{CH}_2)_2\text{CO}-$ or $-\text{CO}(\text{CH}_2)_3\text{CO}-$, or (3) an acyl group derived from an aromatic dicarboxylic acid, especially a dicarboxylic acid of the benzene series such as isophthalic acid or terephthalic acid, and, in addition, pyridine dicarboxylic acid or furan dicarboxylic acid.

The following dyes have proved to be especially suitable:

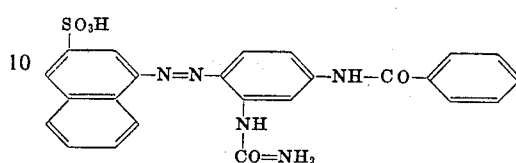


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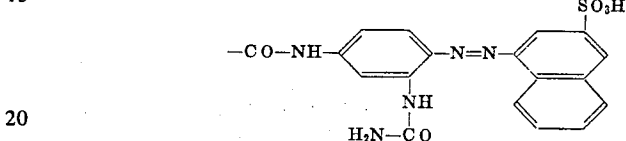
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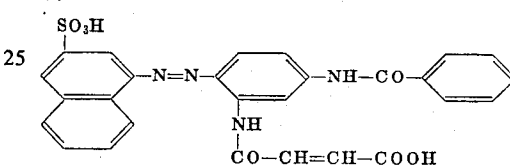
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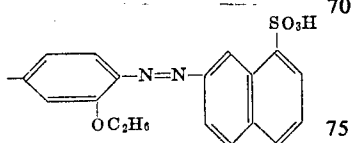
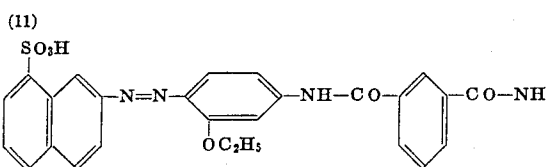
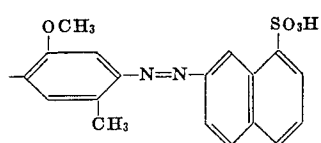
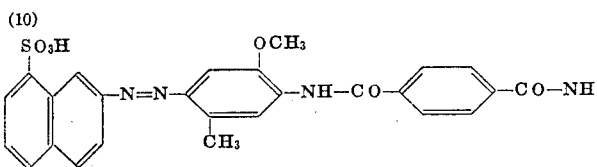
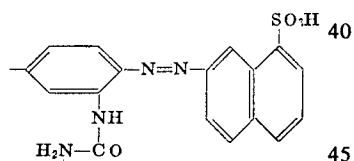
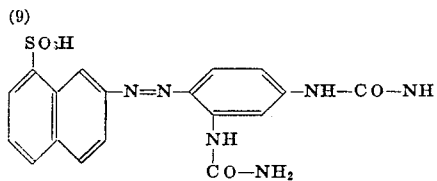
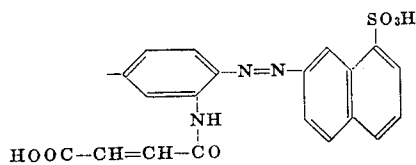
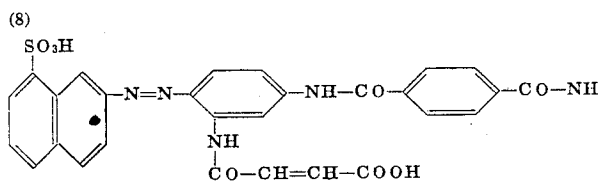
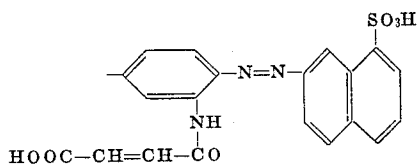
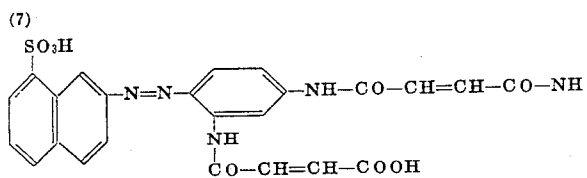
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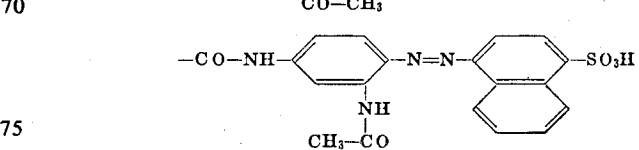
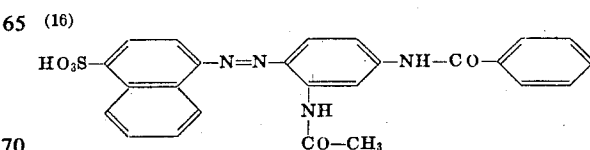
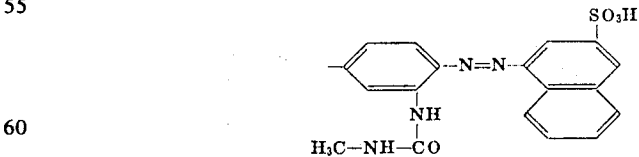
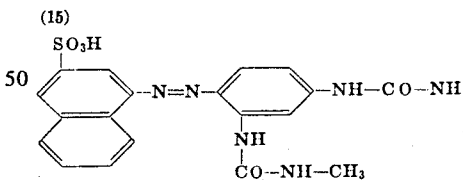
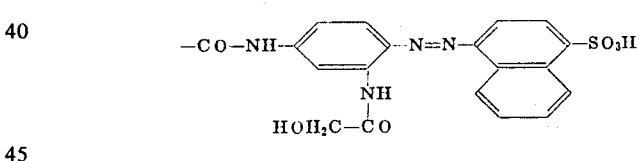
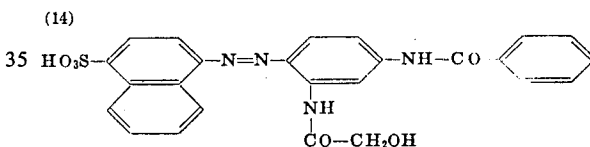
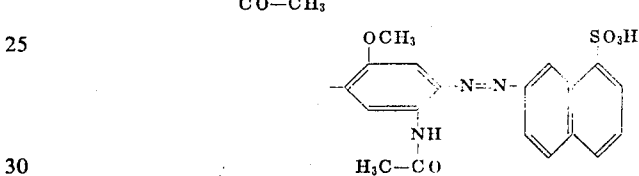
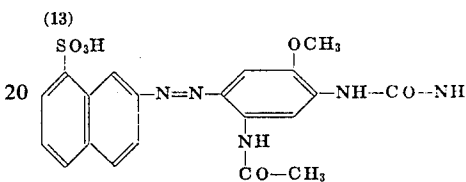
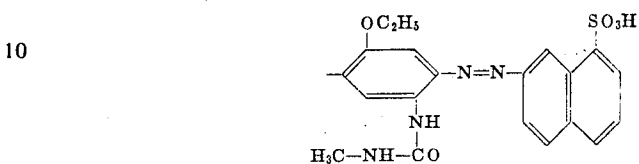
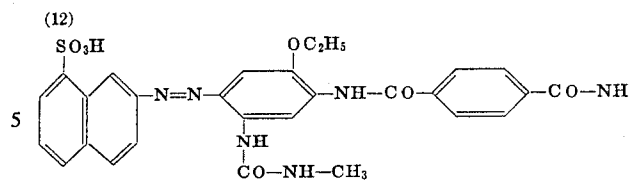
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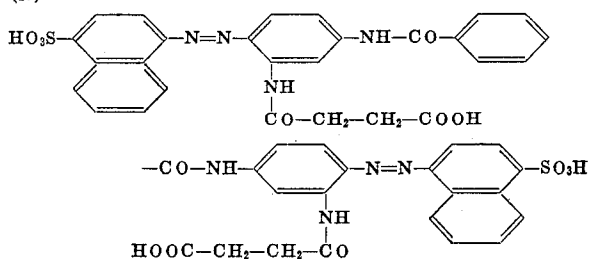


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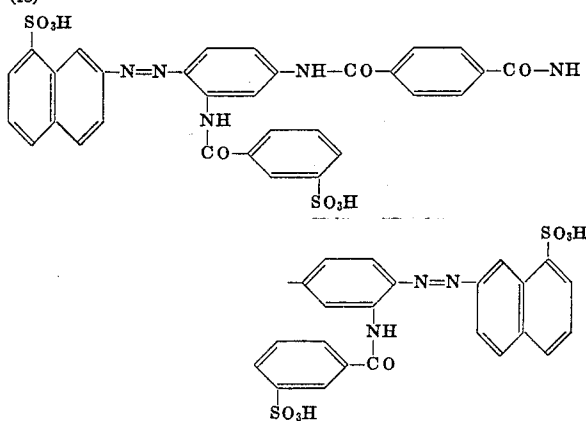


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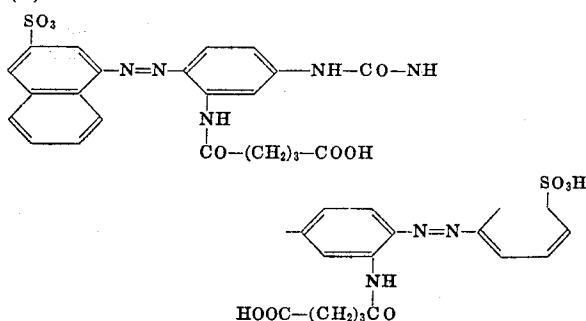
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The dyes which are to be used according to the invention are prepared by known methods. For example, the dyes are prepared by first coupling diazotized amino arylsulfonic acids with 1-amino-3-acylamino benzene compounds, reference is made to U.S. Pat. No. 3,480,438 columns seven to nine. The resulting amino azo compound is reacted with phosgene or a dicarboxylic acid chloride, such as phthalic acid chloride, or a fumaric acid chloride. Reference is made to column nine of U.S. Pat. No. 3,480,438 for reaction with phosgene. Reference is made to U.S. Pat. No. 2,813,856 for reaction of amino azo dyes with fumaric acid chloride. Reference is also made to Houben/Weyl, "Methoden der organischen chemie" fourth Edition, Volume X/3, page 398.

A special advantage of these dyes over known dyes of similar constitution is the ease with which they can be made in a particularly pure form so that problems caused by impurities are avoided. The spectral properties, as well as the brilliance of the dyes, are excellent. Because of the outstanding compatibility with silver halide gelatin emulsions the dyes can be easily incorporated in the layers and a very uniform distribution of the dyes is thus achieved. Many other azo dyes which are spectrally suitable are inoperative because they are unsatisfactory in respect of the latter properties.

On account of their excellent properties, the dyes according to the invention can be applied in color photographic layers for the silver-dye-bleach process in various ways. As will be seen from the following examples, they are preferably employed as image dyes in layers which are subjected to a simple

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black-and-white development and thus form in the subsequent dye bleaching bath in a direct positive dye image. However, it is also possible to carry out a black-and-white reversal development, whereby after treatment with common dye-bleaching baths, dye images with a gradation opposite to the original are obtained.

The dyes are substantially inert to agents customarily added to photographic layers, such as stabilizers, sensitizing dyes, chemical sensitizers, plasticizers, wetting agents, hardeners and the like.

As shown in the following example, they can be bleached out to pure whites in different types of bleaching baths, such as those which are based on quinoline and iodide, as described in U.S. Pat. No. 2,629,568 (example 29) or thiourea (as indicated in British Pat. No. 507,211) and with different bleaching catalysts, such as quinoxalines or phenazine derivatives.

They can be applied onto any suitable supports, such as glass, baryta-coated papers, papers of all types which have been made water repellent, such as polyethylene-coated papers, cellulose acetate or polyesters and polycarbonate films and pigmented cellulose acetate films.

The image whites are also not discolored by exposure to light over long periods.

EXAMPLE I

400 ml. of a 4 percent gelatin solution containing 4.5 g. of dye 1 and 0.7 g. of saponin, are added to 800 ml. of a melted silver bromide gelatin emulsion. After the addition of 20 ml. of a 1 percent aqueous solution of tris-acryloylhexahydrotriazine as hardening agent one sample of the emulsion is applied onto a support of baryta-coated paper and another on to a support of cellulose triacetate in a thickness which corresponds to a silver application of 0.6 to 0.9 g. of silver per m².

A strip of each of the dried materials is exposed in a sensitometer customarily employed in the art behind a grey step wedge, using yellow or white light. The exposed samples are processed as follows:

1. Development: 5 minutes in the following developer solution:

p-methylaminophenol	1 g.
hydroquinone	3 g.
anhydrous sodium sulfite	13 g.
sodium bromide	1 g.
anhydrous soda	26 g.
water to 1,000 ml.	

2. Rinsing: 5 minutes.

3. Fixing: 5 minutes in the following bath:

sodium thiosulfate cryst.	200 g.
potassium metabisulfite	20 g.
water up to 1,000 ml.	

4. Rinsing: 5 minutes.

5. Hardening: 5 minutes in the following bath:

formaldehyde (30% aqueous solution)	100 ml
sodium bicarbonate	2 g.
water up to 1,000 ml.	

6. Rinsing: 5 minutes

7. Dye bleaching: 15 minutes in the following bath:

potassium iodide	10 g.
sodium hypophosphite	10 g.
sulfuric acid conc.	75 ml.
quinoline	50 ml.
water up to 1,000 ml.	

8. Rinsing: 5 minutes.

9. Bleach fixing: 10 minutes in the following bath:

tetrasodium methylene diamine	26 g.
tetraacetate	24 g.
anhydrous soda	15 g.
ferric chloride	13 g.
anhydrous sodium sulfite	200 g.
sodium thiosulfate	
water up to 800 ml.	

10. Final rinsing: 15 minutes.

After drying, pure yellow dye wedges with high brilliance and good whites are obtained. The test wedges show no dye diffusion and have excellent light fastness. The layers are eminently suitable for use in the production of the yellow partial image in a multilayer photographic material.

EXAMPLE 2

The same procedure is employed as in example 1 but using 4.8 g. of dye 5. After exposure and processing as in example 1, baths one to six, the process is continued as follows:

7. Dye bleaching: 5 minutes in the following bath:

thiourea	28 g.
potassium bromide	18 g.
2-amino-3-hydroxyphenazine	3 mg.
hydrochloric acid conc.	200 ml.
water up to 4,000 ml.	

8. Rinsing: 5 minutes.

9. Bleaching: 5 minutes in the following bath:

copper chloride	25 g.
hydrochloric acid conc.	10 ml.
water up to 1,000 ml.	

10. Fixing: 5 minutes as described in example 1, bath number three.

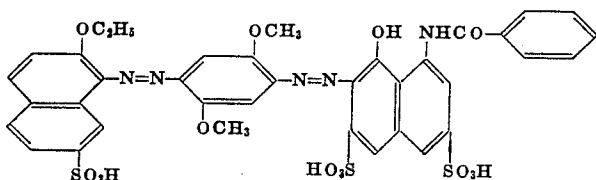
11. Final rinsing: 15 minutes.

After drying, a result very similar to that of example 1 is obtained.

EXAMPLE 3

A color photographic multilayer material for use in the silver-dye-bleach process is prepared as follows: The following layers are applied successively on a support of baryta-coated paper:

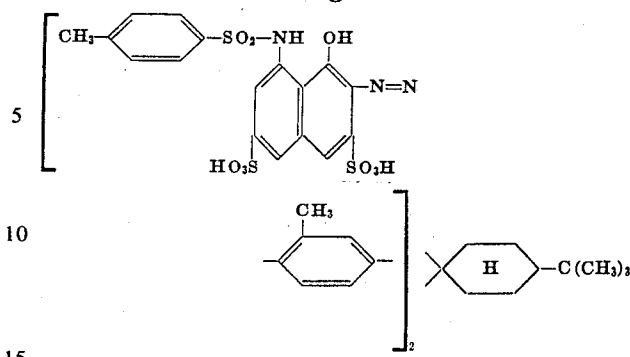
1. A red sensitized layer which contains, for every 500 g. of silver bromoiodide emulsion, (5 mol percent of silver iodide) 12 mg. of the sensitizer of example 11 of German Pat. No. 1,177,481 and 2.7 g. of the following formula:



the preparation of which is described in French Pat. No. 1,471,787, dissolved in 200 ml. of a 2 percent gelatin solution which in addition contains 10 ml. of a 1 percent aqueous solution of N,N',N''-tris-acryloylhexahydrotriazine as hardener and 0.5 g. of saponin. The silver was applied in a quantity of 0.8 g./m² in the form of silver halide.

2. An intermediate layer of 2 percent gelatin solution.
3. A green-sensitive layer which contains, for every 500 ml. of the same silver bromo iodide emulsion, 15 mg. of the sensitizer of example 2 of German Pat. No. 1,177,481 and 2.5 g. of the dye of the following formula:

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the preparation of which is described in German Pat. No. 1,039,840, dissolved in 200 ml. of a 2 percent gelatin solution which in addition contains 10 ml. of a 1 percent aqueous solution of N,N',N''-trisacryloylhexahydrotriazine as hardener as well as 0.4 g. of saponin. The silver is applied in a quantity of 0.75 g./m² in the form of the silver halide.

4. An intermediate layer of a 4 percent gelatin solution to which 8 g. of tartrazine are added per liter.

5. A nonsensitized silver bromide emulsion layer of the type use in example 1.

6. A protective layer of 2 percent gelatin solution.

After drying, the material is exposed behind a multicolored transparency and processed in the manner described in example 1, with the difference that the treatment time in the dye-bleaching bath is increased to 25 minutes. A color-photographic image in true colors is obtained.

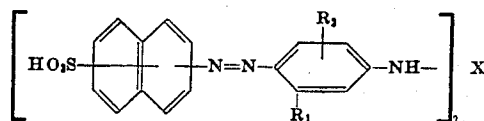
EXAMPLE 5

The procedure is the same as that described in example 4 with the difference that the tartrazine-containing gelatin layer between the green sensitized layer and the nonsensitized emulsion layer is replaced by an arrangement of layers as follows:

1. An intermediate layer of a 2 percent gelatin solution
 2. A filter layer of a 2 percent gelatin solution which contains silver filter yellow having a density of 0.3 for a layer thickness of 1 micron and 0.3 g. of dye 5.
 3. An intermediate layer of a 2 percent gelatin solution.
- After drying, exposure and processing as described in example 4, a color-photographic image of the original with particularly brilliant color tones is obtained.

We claim:

1. A light-sensitive silver-dye-bleach silver halide emulsion layer containing a bis-azo dye of the following formula:



in which

R₁ represents hydrogen, chlorine, bromine alkyl, having up to three carbon atoms, acylamino or an ureido group;

R₂ represents hydrogen, chlorine bromine alkyl having up to three carbon atoms or alkoxy having up to three carbon atoms and

X represents carbonyl or the acyl group of a saturated or unsaturated aliphatic dicarboxylic acid or of an aromatic dicarboxylic acid.

2. The light-sensitive emulsion of claim 1, wherein R₁ represents an acylamino group, the acyl radical of which is derived from a saturated or unsaturated monobasic or dibasic aliphatic carboxylic acid which has up to six carbon atoms.

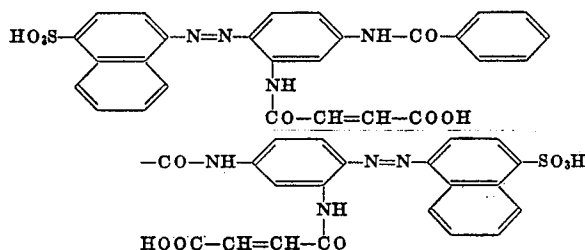
3. The light-sensitive emulsion of claim 1, wherein R₁ represents an ureido group.

4. The light-sensitive emulsion of claim 1, wherein X represents carbonyl or acyl derived from a benzene dicarboxylic acid.

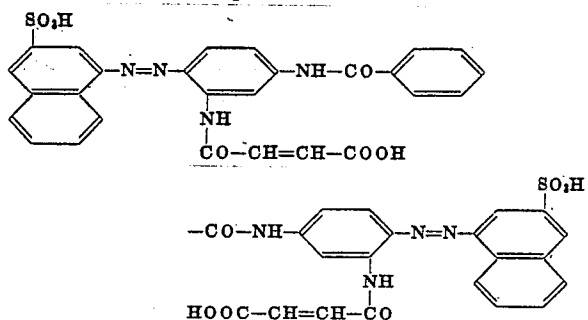
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5. The light-sensitive emulsion of claim 1, wherein X stands for acyl derived from an olefinically unsaturated dicarboxylic acid.

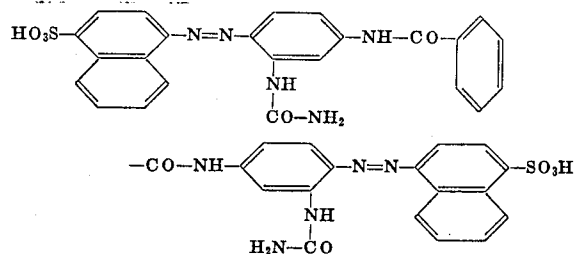
6. The light-sensitive emulsion of claim 4, wherein the bis-azo dye has the following formula:



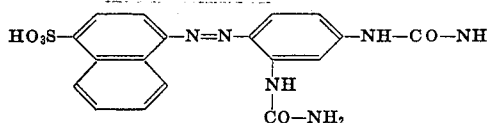
7. The light-sensitive emulsion of claim 4, wherein the bis-azo dye has the following formula:



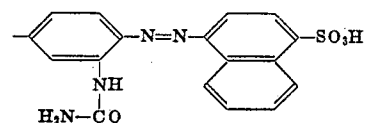
8. The light-sensitive emulsion of claim 4, wherein the bis-azo dye has the following formula:



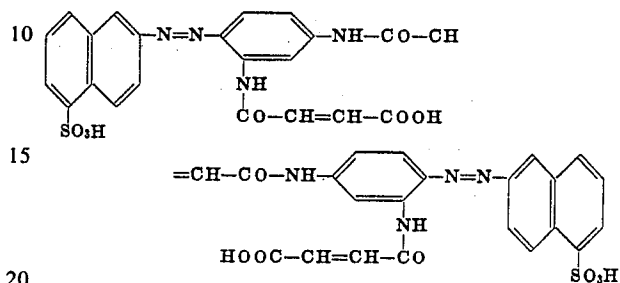
9. The light-sensitive emulsion of claim 4, wherein the bis-azo dye has the following formula:



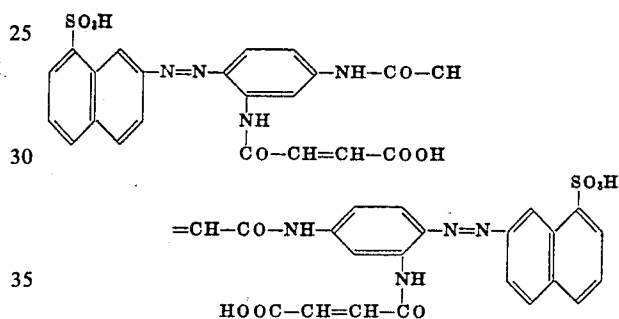
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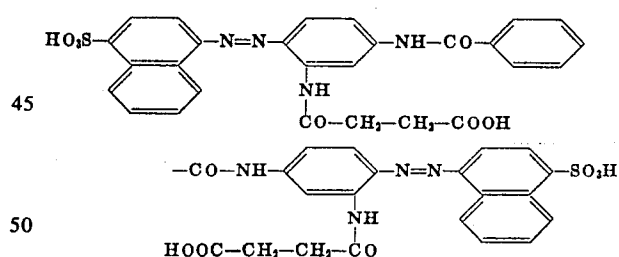
10. The light-sensitive emulsion of claim 5, wherein the bis-azo dye has the following formula:



11. The light-sensitive emulsion of claim 5, wherein the bis-azo dye has the following formula:



12. The light-sensitive emulsion of claim 4, wherein the bis-azo dye has the following formula:



* * * * *

55

60

65

70

75

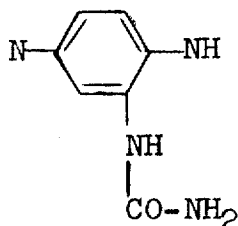
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,582 Dated October 26, 1971

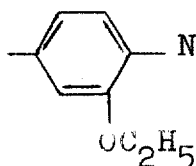
Inventor(s) Hans Vetter et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 65, the left hand portion of the formula should read as follows: $-\text{COCH}=\text{CHCO}$;
Column 2, line 14 of formula (2) should read as follows; on the middle ring:



Column 3, line 75 of formula (11), the left hand portion of the formula should read as follows:



Column 6, line 2, delete the word "in";
Column 7, line 2 should read as follows:
-- tetrasodium ethylene diamine -- ;
Column 7, line 54, after "2.7 g" insert -- of the dye -- ;
Column 8, line 25, "used" instead of -- use -- ;

Signed and sealed this 29th day of August 1972.

(s)
A

HOWARD M. FLETCHER, JR.
Assistant Officer

ROBERT GOTTSCHALK
Commissioner of Patents