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COLOUR PHOTOGRAPHY

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5 Claims. (Cl. 96—53)

This invention relates to colour photography and particularly to the silver-dye-bleach process of colour photography.

This important method of producing colour records is based on the following general procedure. A photographic silver halide emulsion layer, usually a gelatino silver halide emulsion layer, includes as a uniform dispersion therein, a suitable dyestuff. The layer is exposed to light or otherwise rendered developable so that a latent silver image is formed therein. This image is developed to a silver image. The layer is then treated with a "bleach" bath which has the effect of oxidising the silver image and simultaneously reducing (or bleaching) the dyestuff in the region of the silver image. The silver salts and any residual silver are then removed from the layer and the layer then contains only a dyestuff image which is complementary in sign to the original silver image.

Considerable variations are possible in this process. For example, the layer may be dyed with the dyestuff after the exposure step or after the development of the silver image. Moreover, the dyestuff may be included in a plain gelatin layer coated adjacent to the emulsion layer. A large number of patents have been granted in respect of the process, the main details of which can be ascertained from British patent specification Nos. 397,159 and 397,188.

In order to produce a record in full colour there is generally employed a multilayer material which contains three light-sensitive silver halide emulsion layers, one sensitive to blue light only and the others sensitized to sensitive to blue light only and the other sensitised to layers from recording blue light in addition to the light to which they are sensitised, it is usual to provide a blue-absorbing filter layer between these latter layers and the emulsion which is sensitive only to blue, a common form of assembly being:

(*a*) Support layer
(*b*) Red-sensitive emulsion layer
(*c*) Green-sensitive emulsion layer
(*d*) Blue-absorbing filter layer
(*e*) Blue-sensitive emulsion layer

Layer (*d*) is not always essential since layer (*e*), when dyed yellow, may provide a sufficient barrier to blue light.

Polychromatic light incident on layer (*e*) causes the formation of latent silver images in layers (*e*), (*c*) and (*b*), respectively recording in those layers the blue, green and red sensations of the exposing light.

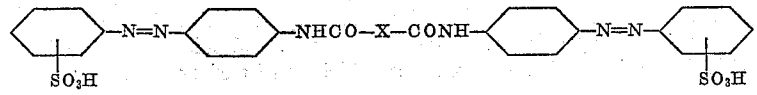
In the silver-dye-bleach process as ordinarily practised, layer (*b*) is dyed blue-green (cyan), layer (*c*) is dyed magenta and layer (*e*) is dyed yellow. Accordingly, when the material is exposed, developed to form silver images and subjected to the required bleaching treatment and treated to remove residual silver salts and silver, the final product carries "positive" yellow, magenta and cyan images complementary to the "negative" silver images formed on development, so that when viewed it

provides an accurate representation of the original subject of the exposure.

One of the principal difficulties in the silver-dye-bleach process is the selection of suitable dyestuffs for the purpose. Some hundreds of dyestuffs have been suggested, but most of the dyestuffs proposed are unsatisfactory in one or more respects. A principal difficulty is to ensure that the dyestuff employed will not diffuse from the gelatin emulsion layer in which it is incorporated, and various proposals, such as mordanting, have been made to overcome this difficulty. In selecting dyestuffs for use, moreover, it is desirable that they should be bleached rapidly by the bleaching baths employed and also preferable that their inclusion in the emulsion layer should not too seriously reduce the sensitivity of the emulsion. In addition, of course, it is desirable that the dye should approach as closely as possible to the theoretical requirement that, of red, blue and green light it should absorb all of one while fully transmitting or reflecting both of the others.

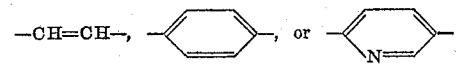
It is an object of the present invention to provide a new class of yellow dyestuffs for use in the silver-dye-bleach process which approach more closely to the desiderata set forth above.

According to the present invention a process for the production of a yellow dyestuff image in a photographic layer comprises including in a light-sensitive gelatino silver halide emulsion layer, or in a plain gelatin layer coated adjacent thereto, a yellow dyestuff of the formula:



where X is an unsaturated aliphatic, aromatic or heterocyclic divalent radicle, or of the said formula in which the various benzene rings carry non-ionogenic substituents or of the said formula in which the terminal benzene rings each carry one carboxylic acid group, the dyestuff being symmetrical about the bridging group X, forming a latent silver image in said layer, developing said image, subjecting the developed image to treatment which bleaches or removes the silver image and simultaneously bleaches the dyestuff in situ therewith, and removing any residual silver and silver salts from the product.

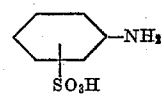
The group X may be, for example,



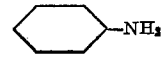
Suitable non-ionogenic substituents are alkyl, e.g. methyl or ethyl, alkoxy, e.g. methoxy or ethoxy, acylamino, e.g. acetylamino groups or halogen atoms, particularly chlorine.

The precise hue of the dyestuff varies with the substituents present and their position. Generally, alkyl or alkoxy groups on the intralinear benzene rings in meta position to the azo linkages tend to yield dyes of more lemon a shade, while the same groups in ortho position to the azo linkages tend to yield dyes of more orange a shade. Halogen atoms in these intralinear benzene groups tend to produce more lemon shades.

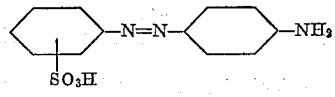
Methods for the production of the foregoing class of dyestuffs are exemplified later herein. In general terms they are prepared by diazotising a compound of the formula:



(which may contain further, non-ionogenic, substituents), coupling it with a compound of the formula:



(which may contain further, non-ionogenic, substituents) to produce a monoazo dyestuff of the formula:



and treating that dyestuff with an acylating agent of the formula:

$$Y—CO—X—CO—Y$$

where Y is hydroxyl or halogen, or the two Y groups together represent an oxygen atom, the compound then being an anhydride.

Further, according to the invention a process of colour photography comprises a process as just set forth in which the gelatino silver halide layer is blue-sensitive and constitutes one of the layers of a multilayer photographic material which further contains photographic emulsion layers sensitive to green and red light respectively dyed with magenta and cyan dyestuffs, and the said yellow dyestuff is included in said blue-sensitive layer or in a plain gelatin layer coated adjacent thereto. More particularly the invention provides a process in which the said yellow dyed layer is layer (*e*) of an assembly consisting of:

(*a*) Support layer
(*b*) Red-sensitive emulsion layer dyed cyan
(*c*) Green-sensitive emulsion layer dyed magenta
(*d*) Blue-absorbing filter layer
(*e*) Blue-sensitive emulsion layer dyed yellow

optionally with plain colloid separating layers between some or all of the adjacent layers recited.

The invention further includes such light-sensitive materials employed in the aforesaid processes, and suitable for variants of those processes, which consist of or include a gelatino silver halide emulsion layer containing a yellow dyestuff as above set forth.

Specific dyestuffs which have been found to be of particular value are set forth in the examples which follow.

The bleaching of the yellow dyestuffs employed in this invention can be effected by any of the types of bleaching bath commonly employed in the silver-dye-bleach process.

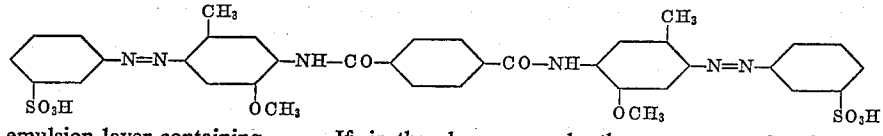
The plain use of acid, e.g. hydrobromic or hydrochloric, is effective but is very slow. The inclusion of halide salts has an accelerative effect, but these bleaching baths are still slow. The inclusion of a solvent for silver halide such as thiourea or pyridine has a strongly accelerative effect, and this can be greatly increased by the inclusion of an accelerating substance or catalyst. In these connections reference may be made to British patent specifications Nos. 397,159 and 490,451 for suitable bleaching baths.

The following illustrate suitable dyestuffs according to the invention, and their preparation:

PREPARATION OF THE DYESTUFFS

Dyestuff No. 1.—32.1 parts of the aminomonoazo dyestuff obtained by coupling diazotised 1-aminobenzene-3-sulphonic acid with 1-amino-2-methoxy-5-methylbenzene, are dissolved at 50–55° with the addition of sodium carbonate so that the solution has a neutral reaction. After cooling to 20–25°, a solution of 11.3 parts of benzene-1.4-dicarboxylic acid dichloride in 60 parts of acetone and an aqueous solution of sodium carbonate are so added dropwise together that the reaction product always has a neutral reaction. As soon as no more free amino can be traced, the disazo dyestuff formed is precipitated by the addition of sodium chloride. It is filtered off, washed with diluted sodium chloride solution and dried. It is a yellow powder which dissolves in water with a yellow colour and which dyes gelatin in orange-yellow shades.

The free acid of the dyestuff corresponds to the formula:

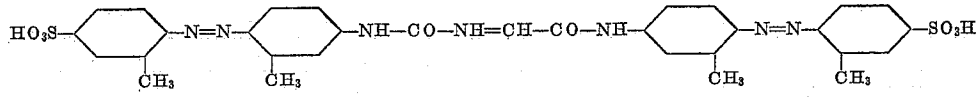


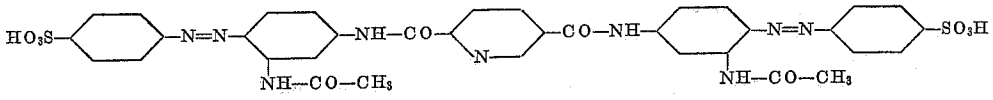
If, in the above example, the components for the formation of the aminomonoazo dyestuff or of the acylating agent are altered according to the following table, then dyestuffs are obtained which have similar properties.

Table I

Dyestuff No.	Diazo Component	Coupling Component	Acylating Agent	Gelatin Dyeing Shade	Aqueous Solution Shade	Colour of Powder
2	1-aminobenzene-3-sulphonic acid.	1-amino-2-methoxy-5-methylbenzene.	benzene - 1.3 - dicarboxylic acid dichloride.	orange-yellow	orange	yellow-brown.
3	do	1-amino-3-acetylaminobenzene.	benzene - 1.4 - dicarboxylic acid dichloride.	lemon-yellow	lemon-yellow	yellow.
4	do	do	benzene - 1.3 - dicarboxylic acid dichloride.	do	yellow	yellow-brown.
5	do	1-amino-2-methoxybenzene	benzene - 1.4 - dicarboxylic acid dichloride.	yellow	orange-yellow	orange.
6	do	1-amino-3-methylbenzene	do	do	do	yellow-brown.
7	1-amino-2-methylbenzene-4-sulphonic acid.	1-amino-3-acetylaminobenzene.	do	lemon-yellow	yellow	yellow.
8	1-amino-4-methylbenzene-2-sulphonic acid.	1-amino-2-methoxy-5-methylbenzene.	do	orange-yellow	orange	orange.
9	1-amino-3-methylbenzene-4-sulphonic acid.	1-amino-3-carbomethoxyaminobenzene.	benzene - 1.3 dicarboxylic acid dichloride.	lemon-yellow	yellow	yellow-brown.
10	1-amino-2-methoxybenzene-5-sulphonic acid.	1-amino-3-methylbenzene	benzene - 1.4 dicarboxylic acid dichloride.	yellow	do	yellow.
11	1-amino-3-methoxybenzene-4-sulphonic acid.	1-amino-2-methoxybenzene	do	orange-yellow	orange	orange.
12	1-amino-2.4-dimethylbenzene-6-sulphonic acid.	1-amino-3-carbomethoxyaminobenzene.	do	yellow	orange-yellow	Do.
13	1-amino-4-chlorobenzene-5-sulphonic acid.	1-amino-3-acetylaminobenzene.	do	do	yellow	yellow-brown.
14	1-amino-5-chlorobenzene-2-sulphonic acid.	do	do	lemon-yellow	lemon-yellow	yellow.
15	1-amino-4-methylbenzene-2-sulphonic acid.	do	do	yellow	yellow	Do.
16	1-amino-4-hydroxybenzene-3-carboxylic acid-5-sulphonic acid.	1-amino-3-methylbenzene	do	orange-yellow	orange	orange.
17	1-aminobenzene-3-sulphonic acid.	1-amino-3-methoxybenzene	2.5-dichlorobenzene-1.4-dicarboxylic acid dichloride.	yellow	yellow	yellow-brown.
18	1-aminobenzene-4-sulphonic acid.	1-amino-3-carbomethoxyaminobenzene.	do	lemon-yellow	do	yellow.

Dyestuff No. 19.—33.4 parts of the aminomonazo dyestuff 1-amino-benzene-4-sulphonic acid→1-amino-3-actylaminobenzene are dissolved with a neutral reaction with the addition of sodium hydroxide in 500 parts of water. 11.4 parts of pyridine-2.5-dicarboxylic acid dichloride dissolved in 60 parts of dioxan are slowly added dropwise at 40–45°. The hydrochloric acid which is split off during the reaction is continuously made neutral by the simultaneous addition dropwise of caustic soda lye. As soon as no more aminomonoazo dyestuff can be traced, the disazo dyestuff formed is precipitated by the addition of sodium chloride, filtered off and washed with diluted sodium chloride solution. After drying, it is a yellow-brown powder which dissolves in water with a yellow colour and dyes gelatin in lemon-yellow shades. The new dyestuff corresponds to the formula:



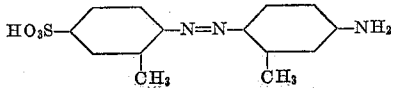


If, in the above example, the 33.2 parts of the aminomonoazo dyestuff are replaced by a corresponding number of parts of one of the monoazo dyestuffs given in the following table, or if the acylating agent is replaced by a corresponding number of parts of one of the acid halides given in the following table, then dyestuffs are obtained which have similar properties.

Table II

Dyestuff No.	Diazo Component	Coupling Component	Acylating Agent	Gelatin Dyeing Shade	Aqueous Solution Shade	Colour of Powder
20	1-aminobenzene-4-sulphonic acid.	1-amino-2-methoxy-5-methylbenzene.	pyridine-2.5-dicarboxylic acid dichloride.	orange-yellow	orange	red-orange.
21	1-aminobenzene-3-sulphonic acid.	1-amino-3-methylbenzene	pyridine-2.4-dicarboxylic acid dichloride.	lemon-yellow	yellow	yellow.
22	do	1-amino-3-acetylaminobenzene.	pyridine-2.6-dicarboxylic acid dichloride.	do	do	Do.
23	1-aminobenzene-2-sulphonic acid.	1-amino-2-methoxybenzene	pyridine-3.5-dicarboxylic acid dichloride.	yellow	do	Do.
24	1-amino-2-methylbenzene-4-sulphonic acid.	1-amino-3-carbomethoxyaminobenzene.	pyridine-2.4-dicarboxylic acid dichloride.	do	do	Do.
25	1-amino-4-methylbenzene-2-sulphonic acid.	1-amino-3-methoxybenzene	thiophene-2.5-dicarboxylic acid dichloride.	orange-yellow	orange	orange.
26	1-amino-3-methylbenzene-4-sulphonic acid.	1-amino-2-methoxy-5-methylbenzene.	thiophene-2.4-dicarboxylic acid dichloride.	orange	do	red.
27	1-amino-2-methoxybenzene-5-sulphonic acid.	1-amino-3-carbomethoxyaminobenzene.	thiophene-2.5-dicarboxylic acid dichloride.	orange-yellow	do	yellow-brown.
28	1-amino-3-methoxybenzene-4-sulphonic acid.	1-amino-3-methylbenzene	furan-2.5-dicarboxylic acid dichloride.	yellow	yellow	yellow.
29	1-amino-5-chlorobenzene-2-sulphonic acid.	1-amino-2-methylbenzene	furan-2.5-dicarboxylic acid chloride.	lemon-yellow	do	yellow-brown.
30	1-amino-4-hydroxybenzene-3-carboxylic acid-5-sulphonic acid.	1-amino-3-methylbenzene	pyrrole-2.5-dicarboxylic acid dichloride.	orange	orange	red.

Dyestuff No. 31.—30.5 parts of the aminomonoazo dyestuff of the formula:



which is obtained is precipitated by the addition of sodium chloride, filtered off and washed with diluted sodium chloride solution. The dried dyestuff is a yellow powder which dissolves in water with a yellow colour and has a very good affinity to gelatin.

If, in the above example, the 8.5 parts of fumaric acid dichloride are replaced by the corresponding number of parts of maleic acid dichloride, methyl fumaric acid dichloride, methyl maleic acid dichloride, bromofumaric acid dichloride, chlorofumaric acid dichloride, butadiene-1.4-dicarboxylic acid dichloride, or if the 30.5 parts of the aminomonoazo dyestuff are replaced by the corresponding number of parts of one of the aminomonoazo dyestuffs listed in the following table, then dyestuffs with similar properties are obtained.

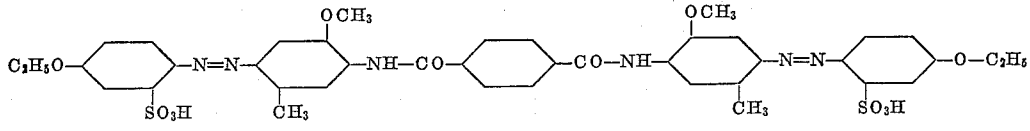
In the following table, fumaric acid dichloride is used as acylating agent in each case.

Table III

Dyestuff No.	Diazo Component	Coupling Component	Gelatin Dyeing Shade	Aqueous Solution Shade	Colour of Powder
32	1-amino-4-methylbenzene-2-sulphonic acid	1-amino-3-acetylaminobenzene	yellow	yellow	orange.
33	1-amino-3-methylbenzene-4-sulphonic acid	1-amino-2-methoxybenzene	lemon-yellow	do	yellow.
34	1-aminobenzene-3-sulphonic acid	1-amino-2-methyl-5-acetylaminobenzene	yellow	do	Do.
35	do	1-amino-3-acetylaminobenzene	do	do	Do.
36	1-aminobenzene-2-sulphonic acid	1-amino-2-methoxy-5-methylbenzene	orange-yellow	orange	red-orange.
37	do	1-amino-3-carbomethoxyaminobenzene	lemon-yellow	yellow	yellow.
38	1-amino-2-methoxybenzene-5-sulphonic acid	1-amino-2-methoxy-5-methylbenzene	orange-yellow	orange	orange.
39	1-amino-3-methoxybenzene-4-sulphonic acid	1-amino-3-methylbenzene	yellow	yellow	yellow-brown.
40	1-amino-2.4-dimethylbenzene-6-sulphonic acid.	do	lemon-yellow	do	yellow.
41	1-amino-4-chlorobenzene-5-sulphonic acid	1-amino-3-methoxybenzene	do	do	Do.
42	1-amino-5-chlorobenzene-2-sulphonic acid	1-amino-2-methoxy-5-acetylaminobenzene	orange-yellow	orange	red.
43	1-amino-4-hydroxybenzene-3-carboxylic acid-5-sulphonic acid.	1-amino-3-methylbenzene	do	do	yellow-brown

Dyestuff No. 44.—36.5 parts of the aminomonoazo dyestuff obtained by coupling diazotised 1-amino-4-ethoxybenzene-2-sulphonic acid with 1-amino-2-methoxy-5-methylbenzene are dissolved with a neutral reaction in 500 parts of water with the addition of sodium hydroxide. 11.3 parts of benzene-1.4-dicarboxylic acid dichloride dissolved in 200 ccm. of acetone are added dropwise through one dropping funnel and simultaneously an aqueous solution of sodium hydroxide is added through another dropping funnel, both additions being made at 20–25° within 1 hour in such a way that the reaction mixture has always a neutral reaction. As soon as no more aminomonoazo dyestuff can be traced, the disazo dyestuff formed is precipitated by the addition of sodium chloride, filtered off, washed with diluted sodium chloride solution and dried.

The new dyestuff corresponds to the formula:



It is a brown-red powder which dissolves in water with an orange-red colour and it dyes gelatin in orange-yellow shades.

Similar dyestuffs are obtained if, in the above example, equivalent amounts of the compounds listed in the following table are used as components for the formation of the aminomonoazo dyestuff and as acylating agents:

The dried coating is exposed to light to record an image therein and processed at 68° F. as follows:

(1) Develop to a silver image by two minutes' treatment in the following developer:

Metol	gm	0.75
Sodium sulphite, cryst	gm	25
Hydroquinone	gm	3
Sodium carbonate, cryst	gm	40
Potassium bromide	gm	1
Water to 1 litre.		

(2) Rinse 30 seconds.
(3) Fix in 20% sodium thiosulphate for 3 minutes.
(4) Rinse 30 seconds.
(5) Harden in 4% formalin.
(6) Wash 10 minutes.
(7) Dye bleach for 8 minutes in the following bath:

Hydrochloric acid (S.G. 1.19)	cc	100
Potassium bromide	gm	12.5
Thiourea	gm	10
2:3-dimethyl quinoxaline	gm	0.1
Water to 1 litre.		

(8) Wash 5 minutes.

Table IV

Dyestuff No.	Diazo Component	Coupling Component	Acylating Agent	Gelatin Dyeing Shade	Aqueous Solution Shade	Colour of Powder
45	1-amino-4-hydroxybenzene-3-carboxylic acid-5-sulphonic acid.	1-amino-3-acetylaminobenzene.	benzene-1.4-dicarboxylic acid dichloride.	orange	orange-red	yellow-brown.
46	1-aminobenzene-3-sulphonic acid.	1-amino-2-methoxy-5-methylbenzene.	pyridine-2.5-dicarboxylic acid dichloride.	yellow-orange	orange	red.
47	1-amino-4-methoxybenzene-2-sulphonic acid.	do	benzene-1.4-dicarboxylic acid dichloride.	orange	orange-red	Do.
48	1-amino-2-methoxybenzene-5-sulphonic acid.	do	do	do	yellowish red	yellow-brown.

The following example, which for simplicity is concerned only with the treatment of a single layer containing the yellow dyestuff, will serve to illustrate the invention:

EXAMPLE

4.38 gms. of dyestuff No. 1 above and 3.3 gms. of dodecyl sodium sulphate are dissolved in 465 ccs. of water. This dye solution is then added to 330 ccs. of a silver chlorobromide emulsion containing 2.95 gms. of silver as silver halide. The mixture is then coated on film base to give a coating weight of 3.2 mgms. of silver halide (estimated as silver) per square decimeter.

(9) Silver bleach for 5 minutes in the following bath:

Copper sulphate, cryst	gm	100
Sodium chloride	gm	100
Hydrochloric acid, conc	cc	50
Water to 1 litre.		

(10) Wash 5 minutes.
(11) Fix in 20% sodium thiosulphate for 3 minutes.
(12) Wash for 10 minutes and dry.

A reverse image in dye is obtained.

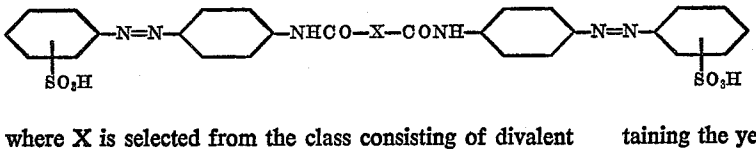
Steps 4 and 5 may be omitted if the original emulsion is hardened or provided with a hardened gelatin supercoat.

Similar results are obtained using the other dyestuffs falling within the formula stated. When the process is repeated with a similar, but undyed, silver halide emulsion, supercoated on the dyed emulsion, it is found by microscopic examination that substantially none of the dyestuff in the dyed layer migrates to the undyed layer either on coating the film or on processing.

All the said dyestuffs are of satisfactory hue, have very good resistance to migration, bleach rapidly and effectively, and are generally of exceptional value in the silver-dye-bleach process of colour photography. Those dyes which absorb more in the visible spectrum, i.e. which appear more orange in colour, are preferred since it is generally possible to obtain adequate image density using a lesser amount of such dyes than is necessary when the lemon-yellow dyes are used.

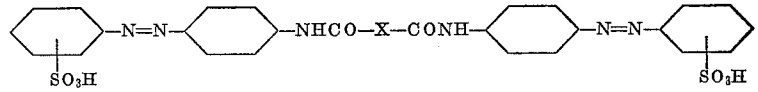
What we claim is:

1. A process for the production of a yellow dyestuff image in a photographic layer which comprises forming a latent image in a light-sensitive gelatino silver halide emulsion layer containing a yellow dyestuff selected from the class consisting of dyestuffs of the formula:



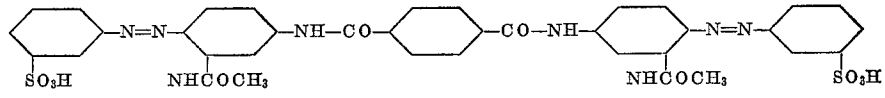
where X is selected from the class consisting of divalent ethylenically unsaturated aliphatic radicles, phenylene radicles and unsaturated divalent heterocyclic radicles, dyestuffs of the said formula in which the various benzene rings carry substituents selected from the class consisting of alkyl groups, alkoxy groups, acylamino groups and halogen atoms and dyestuffs of the said formula in which the terminal benzene rings each carry one carboxylic acid group, the dyestuffs being symmetrical about the bridging group X, developing said image, subjecting the developed silver image to treatment which bleaches the silver image and simultaneously bleaches the dyestuff in situ therewith, and removing any residual silver and silver salts from the product.

2. A light-sensitive gelatino silver halide emulsion containing a yellow dyestuff selected from the class consisting of dyestuffs of the formula:

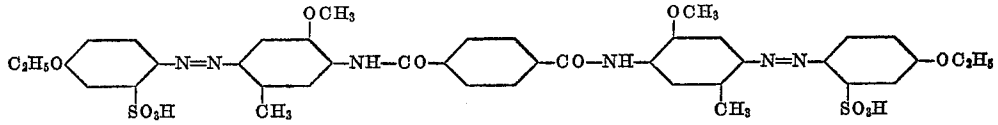


where X is selected from the class consisting of divalent ethylenically unsaturated aliphatic radicles, phenylene radicles and unsaturated divalent heterocyclic radicles, dyestuffs of the said formula in which the various benzene rings carry substituents selected from the class consisting of alkyl groups, alkoxy groups, acylamino groups and halogen atoms and dyestuffs of the said formula in which the terminal benzene rings each carry one carboxylic acid group, the dyestuffs being symmetrical about the bridging group X.

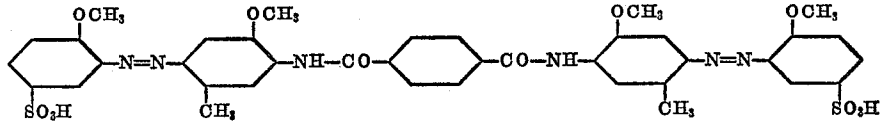
3. A light-sensitive gelatino silver halide emulsion containing the yellow dyestuff of the formula:



4. A light-sensitive gelatino silver halide emulsion containing the yellow dyestuff of the formula:



5. A light-sensitive gelatino silver halide emulsion containing the yellow dyestuff of the formula:



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