

1

2,694,636

LIGHT-SENSITIVE ELEMENT FOR COLOR PHOTOGRAPHY

Ernst Keller, Basel, Switzerland, assignor to J. R. Geigy S. A., Basel, Switzerland, a Swiss company

No Drawing. Application June 27, 1952,
Serial No. 296,078

Claims priority, application Great Britain August 16, 1951

6 Claims. (Cl. 95—6)

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 specifications Nos. 397,159 and 397,188.

In order to produce a record in full colour it is necessary to employ essentially a multilayer material which contains three light-sensitive silver halide emulsion layers, one sensitive to blue light only and the others sensitised to green and red light respectively. To avoid these latter 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.

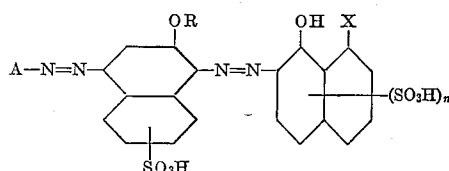
The silver-dye-bleach process, despite its inherent attractiveness, has not achieved any widespread commercial use since in practice various difficulties arise. One of these difficulties is the selection of suitable dyestuffs for the purpose. Some hundreds of dyestuffs have been suggested, but most if not all of the dyestuffs proposed

2

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.

The present invention is concerned with the provision of a new class of dyestuffs for use in the silver-dye-bleach process, which are highly substantive to gelatin and which may be rapidly bleached.

According to the present invention a process for the production of a cyan 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 cyan dyestuff of the formula:



where A is the residue of a diazotised aminophenylbenzyl ether or of a diazotised aminophenyl-phenyl ether which may contain in the benzene rings additional substituents usually found in azo dyestuffs, particularly additional ether groups, but no water-solubilising acid groups, R is a lower alkyl group or a carboxymethyl group, X is a hydroxyl group or an amino, alkylamino, aralkylamino or acylamino group, and n is 1 or 2, forming a latent silver image in said layer, developing said image, subjecting the developed silver 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.

Further according to the invention a process of colour photography comprises a process as just set forth in which the said layer is sensitive to red light and constitutes one of the layers of a multilayer photographic material which further contains photographic emulsion layers sensitive to blue and green light respectively dyed with yellow and magenta dyestuffs, and more particularly the invention provides a process in which the said cyan-dyed layer is layer (b) 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

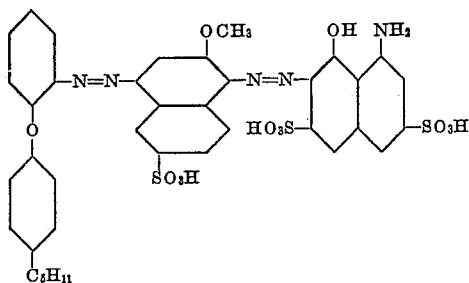
optionally with plain colloid separating layers between some or all of the adjacent layers recited.

The invention further includes the 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 cyan dyestuff as above set forth.

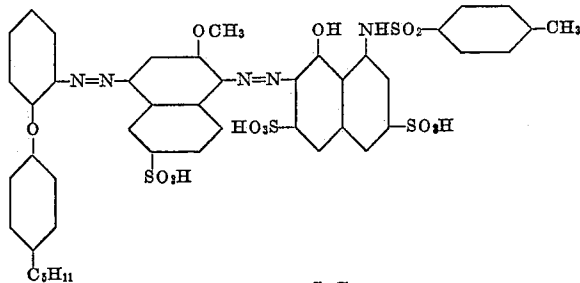
Preferred dyestuffs within the general formula given above are those in which R is a methyl or ethyl group and the sulphonic acid of the middle naphthalene ring is in the 6 or 7 (preferably the 6) position. One of the sulphonic acid groups in the right-hand naphthalene nucleus is preferably in the 4, 5 or 6 position of that nucleus with respect to the 8-hydroxyl group and where a second sulphonic acid group is present it is preferably in the 2, 3 or 4 position depending on the position of the first sulphonic acid group. Preferred positions where two sulphonic acid groups are present are the 3:6 and 2:4 positions.

Specific dyestuffs which have been found to be of greatest value are:

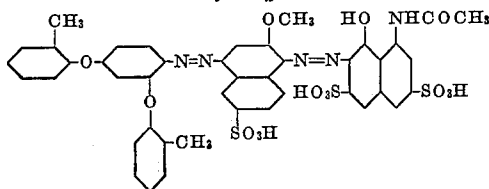
3
Dyestuff A



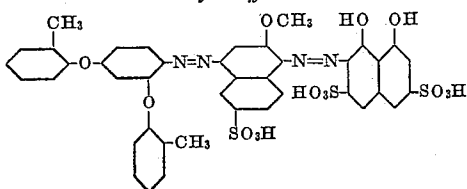
Dyestuff B



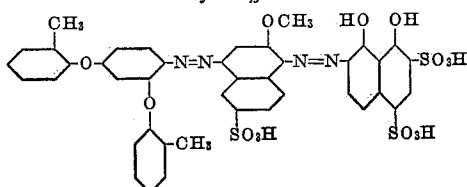
Dyestuff C



Dyestuff D



Dyestuff E



The bleaching of the cyan 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 example, which for simplicity is concerned only with the treatment of a single layer containing the cyan dyestuff, will serve to illustrate the invention.

Example

6 gms. of Dyestuff A above and 5 gms. of dodecyl sodium sulphate are dissolved in 550 ccs. of water by warming. This dye solution is then added to 450 cs. of silver iodobromide emulsion containing 13 gms. of silver as silver halide. The mixture is then coated on film base to give a coating weight of 15 mgms. of silver and 7 mgms. of dye per square decimeter.

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:

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

2. Rinse 30 seconds.

3. Fix in 20% sodium thiosulphate for 3 minutes.

4. Rinse 30 seconds.

15 5. Harden in 4% formalin.

6. Wash 10 minutes.

7. Dye bleach for 8 minutes in the following bath:

	Potassium iodide	gms. 10
20	Pyridine	ccs. 50
	Sodium hypophosphite	gms. 5
	Sulphuric acid	ccs. 75
	Water to 1 litre.	

8. Wash 5 minutes.

25 9. Silver bleach for 5 minutes in the following bath:

	Copper sulphate, cryst	gms. 100
	Sodium chloride	gms. 100
	Hydrochloric acid, conc	ccs. 50
30	Water to 1 litre.	

10. Wash 5 minutes.

11. Fix in 20% sodium thiosulphate for 3 minutes.

12. Wash for 10 minutes and dry.

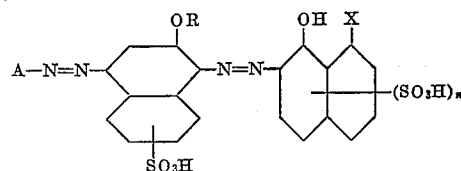
35 A reversed image in dye is obtained.

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, and particularly when using Dyestuffs B, C, D and E above. 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. Processes for the production of the dyestuffs employed in the present invention are described and claimed in co-pending application Serial No. 296,079 filed on even date herewith.

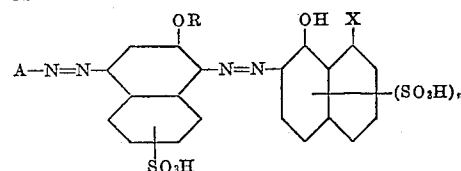
What I claim is:

1. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer thereon and, in contact with said layer, a cyan dyestuff of the formula:



where A is a residue selected from the class consisting of residues of diazotised aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is a group selected from the class consisting of lower alkyl groups and carboxymethyl groups, X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups, and n is selected from 1 and 2.

2. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer thereon containing uniformly dispersed therein a cyan dyestuff of the formula:

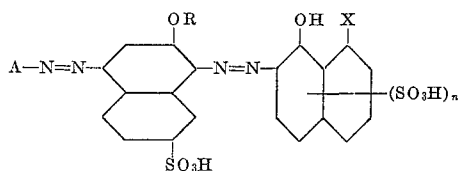


85 where A is a residue selected from the class consisting

5

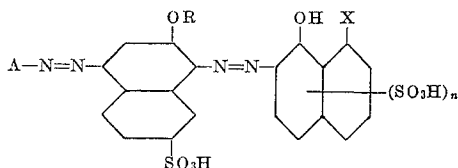
of residues of diazotised aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is a group selected from the class consisting of lower alkyl groups and carboxymethyl groups, X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups, and n is selected from 1 and 2.

3. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer thereon and, in contact with said layer, a cyan dyestuff of the formula:



where A is a residue selected from the class consisting of residues of diazotised aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is selected from methyl and ethyl, X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups, and n is selected from 1 and 2.

4. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer thereon containing uniformly dispersed therein a cyan dyestuff of the formula:

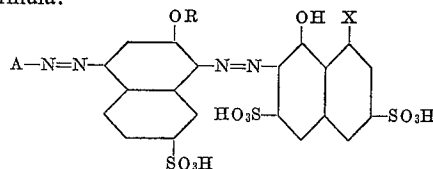


where A is a residue selected from the class consisting of residues of diazotised aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is selected from methyl and ethyl, X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups, and n is selected from 1 and 2.

5. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer there-

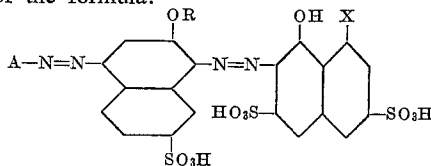
6

on and, in contact with said layer, a cyan dyestuff of the formula:



where A is a residue selected from the class consisting of residues of diazotized aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is a group selected from the class consisting of lower alkyl groups and carboxymethyl groups, and X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups.

6. A photographic element comprising a support, at least one light-sensitive gelatino silver halide layer thereon containing uniformly dispersed therein a cyan dyestuff of the formula:



where A is a residue selected from the class consisting of residues of diazotized aminophenyl-benzyl ether, diazotised aminophenyl-phenyl ether and corresponding ethers which contain in at least one of the benzene rings at least one neutral substituent, R is a group selected from the class consisting of lower alkyl groups and carboxymethyl groups, and X is a group selected from the class consisting of hydroxyl, amino, alkylamino, aralkylamino and acylamino groups.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,326,055	Morris	Aug. 3, 1943
2,420,631	Taylor	May 13, 1947

FOREIGN PATENTS

Number	Country	Date
663,005	Great Britain	Dec. 12, 1951