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PROCESS FOR THE PRODUCTION OF PHOTO-GRAPHIC IMAGES BY THE SILVER DYESTUFF BLEACHING PROCESS AND PHOTOGRAPHIC LAYERS THEREFOR Paul Dreyfuss. Basal S.....

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5,435/60 6 Claims. (Cl. 96-53)

The production of a colored photographic image by the silver dyestuff bleaching method is based on the discovery that an azo dyestuff, one of the wide range of azodyestuffs with which the layer-forming substance, especially gelatine, can be colored, is bleached out depending on the quantity of image-forming silver present in the layer. The silver image is usually produced by exposing the light-sensitive, and in some cases sensitized, silver halide present in the colored layer, and developing and fixing 20 the silver image.

The method can be applied to a colored layer produced by coloring the layer-forming substance with the azodyestuff before the layer is formed or by coloring the finished layer on its support. The method can also be 25

applied to multi-layer photographic materials.

For example, three colored layers may be applied to a transparent or white pigmented support or to baryta paper. Next to the support there is, for example, a selectively red sensitized silver bromide emulsion colored with 30 a green-blue dyestuff, then on this layer there is a selectively green sensitized silver bromide emulsion colored purple, and finally a selectively blue sensitive layer colored yellow. By copying an original color picture (an integral or additive copy) with an ordinary light source, for example, an incandescent tungsten electric lamp or copying color component record with selectively colored light, the silver bromide is exposed at the appropriate areas of the layers. After the exposure the development with ordinary developers, and the fixing, each of the colored layers con- 40 tains a component color record in the form of a negative silver image in a homogeneously colored layer.

By means of a suitable dyestuff bleaching bath, for example, an acid aqueous solution of potassium bromide and thiourea, and a suitable catalyst, such as amino- 45 hydroxy-phenazine, azo-dyestuff present in each layer is bleached out in accordance with the image, so that, in dependence on the quantity of image silver present (and in the simplest case approximately in proportion to the quantity of such silver), the azo dyestuffs are reduced to 50 practically colorless decomposition products according to the following equation:

the following equation:  

$$R_1$$
—N=N— $R_2$ +4Ag+4HBr $\rightarrow$   
 $R_1$ —NH<sub>2</sub>+H<sub>2</sub>N— $R_2$ +4AgBr

R<sub>1</sub> represents the radical of the diazo-compound obtained from the diazo-component R1-NH2 and R2 represents the radical of the coupling component H-R<sub>2</sub>. By the splitting reaction the diazo-component is regenerated, and an amino-compound  $H_2N-R_2$ , is formed from the radical of the coupling component. In the case of disazo- or polyazo-dyestuffs there are also obtained as fission products diamines, for example:

ucts diamines, for example:

$$R_2$$
—N=N-R<sub>3</sub>-N=N-R<sub>2</sub> $\rightarrow$ 
 $2R_2$ —NH<sub>2</sub>+H<sub>2</sub>N-R<sub>3</sub>-NH<sub>2</sub> 65

As the optical density of one molecular proportion of a highly dispersed azo-dyestuff is many times higher than that of four atomic proportions of silver present in crystal aggregates, there is an increase of contrast when a silver 70 image is converted into a dyestuff image, and this is very often undesirable.

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Attempts have, therefore, been made to reduce the contrast of dyestuff images, that is to say, to produce dyestuff images of which the characteristic H and D curve is flatter, and to modify the shape of this gradation curve in various ways. One such attempt consists in adding to the dyestuff bleaching bath a substance having a weak oxidizing action, for example, tartrazine, which diminishes the ratio of bleached dyestuff to metallic silver present in accordance with the image.

This method is effective, but, when applied to multilayer materials, the gradations of all the partial color images are simultaneously modified. It has also been proposed to incorporate the substance having a weak oxidizing action only in one or some of the emulsion layers and in this way to modify the gradations individually, but hitherto no substance suitable for this purpose has been found.

The present invention is based on the discovery of substances which enable the bleaching yield to be decreased, that is to say, the ratio of bleached dyestuff to metallic silver present to be lowered.

The present invention is concerned with the use of dyestuffs (hereinafter referred to as "supplementary dyestuffs) which, like the dyestuffs (hereinafter referred to as "image dyestuffs") used for image formation, are bleached out in the dyestuff bleaching bath in the presence of metallic silver, but, unlike image dyestuffs, are capable of being destroyed in a treatment bath that follows the dyestuff bleaching bath.

Accordingly the present invention provides a process for the production of color photographic images by the silver dyestuff bleaching method, wherein the contrast obtained by bleaching at least one dyestuff serving for image formation is decreased by the presence during the treatment with the dyestuff bleaching bath of at least one dyestuff which is capable of being bleached in the dyestuff bleaching bath in accordance with the image and is capable of being destroyed in a treatment that follows the dyestuff bleaching bath, and which corresponds to the formula

$$(1) R-N=N-Py$$

in which R represents the radical of a component which is bound to the azo linkage in the 1-position of an aromatic or hetero-cyclic ring and contains in the 2- or 4-position of that ring an electron-donating substituent, and Py represents the radical of a 5-pyrazolone bound in the 4-position to the azo linkage.

A number of dyestuffs of the Formula 1 is known, and these dyestuffs can be obtained by methods in themselves known by coupling diazo-compounds of amines of the formula R-NH2, in which R has the meaning given above, with 5-pyrazolones.

As supplementary dyestuffs there are used in the proc-55 ess, for example, dyestuffs of the formula

$$(2) \qquad \qquad R_1 - N = N - Py$$

in which R1 represents a benzene or naphthalene radical which is bound in the 1-position to the azo linkage and contains in the 2-position or advantageously in the 4position as an electron-donating substituent a hydroxyl or amino group, and Py represents the radical of a 5pyrazolone bound in the 4-position to the azo linkage. Among the dystuffs of the Formula 1 in which the radical R is bound to the azo linkage in the 1-position of a heterocyclic ring (this indication of position is in this case not used in a strict sense, but denotes that the azo linkage and electron-donating substituent are bound to vicinal positions of the heterocyclic ring), there are advantageously used dyestuffs of the formula

$$R_2 - N = N - Py$$

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in which  $R_2$  and Py each represent the radical of a 5-pyrazolone bound in the 4-position to the azo linkage, the radicals  $R_2$  and Py being identical or different from each other.

The pyrazolone radicals Py and/or  $\rm R_2$  may, for example, correspond to the formula

in which R' represents the radical of an aliphatic hydrocarbon of low or high molecular weight, and R" represents an unsubstituted or substituted benzene radical

It is generally of advantage to use a supplementary dyestuff containing at least one acid group imparting solubility in water, for example, a carboxylic acid group or advantageously a sulfonic acid group.

As diazo-components for making the supplementary dyestuffs there may be mentioned, for example, the following amines:

1-amino-4-hydroxybenzene,

1-amino-4-hydroxybenzene-3-sulfonic acid,

1-amino-4-hydroxynaphthalene,

1-amino-4-methylaminobenzene,

1-amino-4-diethylaminobenzene,

1-amino-2-methyl-4-diethylaminobenzene,

1-amino-2-ethoxy-4-diethylaminobenzene,

1-amino-4-(di-β-hydroxyethyl)-aminobenzene,

1-amino-4-dimethylaminobenzene-2-carboxylic acid,

1-amino-4-dimethylaminonaphthalene,

1-amino-4-benzylaminobenzene,

1-amino-4-di-dodecylaminobenzene-2-sulfonic acid,

1-amino-4-phenylaminobenzene,

1-amino-4-thiomorpholinobenzene of the formula

1-amino-2-hydroxy-5-methylbenzene,

1-amino-2-hydroxy-5-chlorobenzene,

1-phenyl-3-methyl-4-amino-5-pyrazolone-4'-sulfonic acid.

As coupling components there may be mentioned the following pyrazolones:

1-phenyl-3-methyl-5-pyrazolone-3'- or 4'-sulfonic acid,

1-phenyl-3-methyl-5-pyrazolone-3'-sulfonic acid amide,

1-phenyl-3-methyl-5-pyrazolone-2':5'-disulfonic acid,

1-[5'-stearoylamino-6'-methylphenyl]-3-methyl-5-

pyrazolone-3'-sulfonic acid,

1-phenyl-3-heptadecyl-5-pyrazolone-4'-sulfonic acid, 1-phenyl-3-[4"-lauroylaminophenyl]-5-pyrazolone-4'-sulfonic acid.

Finally, there may also be mentioned dyestuffs of the Formula 1 which contain in the radical R in ortho- or advantageously para-position to the azo linkage a primary amino group as an electron-donating substituent. These dyestuffs can also be made by methods in themselves known, for example, by coupling a 5-pyrazolone with a diazo-compound of an aromatic amine which contains in ortho- or para-position to the amino group a substituent convertible into an amino group, for example, a nitro or acetylamino group, and subsequently converting the said substituent into a primary amino group. Thus, a nitro group is reduced or an acetylamino group is hydrolysed.

When the supplementary dyestuff is soluble in water and diffuses, it may be present in the dyestuff bleaching bath or in a bath preceding the dyestuff bleaching bath. However, supplementary dyestuffs which are fast to diffusion or have been rendered fast to diffusion by means of a precipitating agent, are preferred. Such dyestuffs are 75

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incorporated in one or more of the emulsions of a multilayer material or in one or more phases of a mixed grain emulsion before the emulsions are cast to make the photographic material.

The quantity of the supplementary dyestuff varies depending on the degree of flattening of the graduation curve to be brought about. The quantity required is generally within the range of 5 to 100 percent calculated on the quantity of image dyestuff.

As image dyestuffs there are used dyestuffs that are decolorizable by metallic silver and are stable in silver bleaching baths, and they are principally azo-dyestuffs. However, there are also useful as image dyestuffs other substances capable of being bleached in accordance with an image such, for example, as diazonium salts or components that yield colored metal complexes, which are converted into dyestuffs after the treatment with the dyestuff bleaching bath. It is preferable to use image dyestuffs which are fast to diffusion and are incorporated with the material before the casting operation. However, image dyestuffs may be used which are incorporated by immersion before the treatment with the dyestuff bleaching bath.

In addition to its flattening effect on the gradation curve 25 of the color image in the dyestuff bleaching bath, the supplementary dyestuff may also have a flattening effect on the gradation curve of the silver image, whereby it produces a dual flattening effect. This additional flattening effect is, probably at least partially, due to the color 30 of the supplementary dyestuff and the optical damping produced thereby. The color of the supplementary dyestuff may be similar to the color of the image dyestuff in the same layer or it may be different from the color of the image dyestuff. However, it is desirable to select  $^{35}$  a supplementary dyestuff which does not absorb in a region of the spectrum for which an underlying layer is sensitized. Thus, in a three-layer material, for example, the layers lying above the red-sensitive layer should contain yellow, yellow-red or red supplementary dyestuffs which allow red light to pass through unhindered.

A typical emulsion layer is produced, for example, by mixing in the appropriate sequence a silver halide (for example silver bromide) emulsion in a colloid (for example gelatine), an image dyestuff fast to diffusion, a supplementary dyestuff fast to diffusion, and the usual additions to emulsions such as optical sensitizers, chemical sensitizers, wetting agents, and then casting the mixture on a support.

In a photographic material produced by casting such 50 layers one upon another a silver image is developed in the usual manner, and bleaching is carried out in a dyestuff bleaching bath in which both the image dyestuff and the supplementary dyestuff are destroyed at the places where silver is present. As different dyestuffs have different capacities for being bleached out in different bleaching baths, for example, the capacity of some dyestuffs is influenced more by the quantity of thiourea, and the capacity of other dyestuffs for being bleached is influenced more by the quantity of catalyst, the composition of the bleaching bath also has an influence on the bleaching ratio of the image dyestuff and the supplementary dyestuff, and therefore on the degree of flattening of the image produced by the supplementary dyestuff. It will therefore be understood that a maximum effect is produced when the composition of the bleaching bath is so chosen that it bleaches the supplementary dyestuff more quickly than the image dyestuff. The intensity of the effect can also be regulated by regulating the duration of the action of the dyestuff bleaching bath either by discontinuing the action of the bath after a predetermined time or by allowing the bleaching bath to act until image dyestuff and metallic silver no longer exist together at any part of the image.

or have been rendered fast to diffusion by means of a precipitating agent, are preferred. Such dyestuffs are 75 metallic silver is converted into silver salt, and simul-

taneously the unattacked supplementary dyestuff is destroyed. For this purpose there are advantageously used ferricyanide baths and especially ferricyanide baths at an alkalinity exceeding the pH-value of 7. Finally, the silver salt is dissolved out in a fixing bath, or the two lastmentioned baths may be combined in a single bath of the type of Farmer's reducer.

It should also be explained with regard to the ferricyanide bath that the decoloration of the supplementary dyestuff takes place more rapidly and completely the higher the pH-value of the ferricyanide bath, but that if the pH-value is too high the image dyestuff may also be attacked. The pH-value of the ferricyanide bath is therefore so chosen that it is sufficiently high to bring about the decoloration of the supplementary dyestuff sufficiently rapidly, but not so high as to affect the image dyestuff.

By this treatment the supplementary dyestuff is completely destroyed with the formation of colorless components or components capable of being removed by washing. Accordingly, there are obtained pure colors formed solely by image dyestuffs and pure whites at the colorless places, which is especially important for color images to be viewed by reflected light. Colorless decomposition products of the supplementary dyestuffs, even when they cannot be removed by washing, exert no disadvantageous effect on the fastness to light of the images or they can be rendered harmless.

As the supplementary dyestuffs are damping dyestuffs their effect on the gradation curve of the silver image is influenced by the nature of the sensitization or, in the case of copying materials, by the wavelength of the copying light. The gradation of the dyestuff image can also be further influenced by the action of the supplementary dyestuff on the bleaching of the image dyestuff. As the supplementary dyestuffs can be incorporated only in one or some of the layers, as it is also possible to use mixtures of supplementary dyestuffs, and as different supplementary dyestuffs may be incorporated in different layers, the present invention enables the partial color images to be very considerably flattened and the shape of the 40 gradation curves to be modified as desired.

The following examples illustrate the invention, the parts and percentages being by weight:

#### Example 1

A. There was cast upon a glass plate measuring 13 by 18 cm. a mixture of 3 ml. of a silver bromide emulsion and 7 ml. of a solution containing 0.28 gram of gelatine and 0.01 gram of the purple dyestuff of the formula

H<sub>2</sub>C-CO-NH

CO-NH OH

H<sub>3</sub>C

CH<sub>3</sub>

CH<sub>4</sub>

CH<sub>2</sub>

CH<sub>2</sub>

CH<sub>2</sub>

CH<sub>2</sub>

CH<sub>3</sub>

CH<sub>3</sub>

CH<sub>4</sub>

CH<sub>3</sub>

CH<sub>4</sub>

CH<sub>3</sub>

CH<sub>4</sub>

CH<sub>3</sub>

CH<sub>4</sub>

CH<sub>4</sub>

CH<sub>4</sub>

CH<sub>4</sub>

CH<sub>5</sub>

B. Upon another glass plate was cast a mixture containing, in addition to the ingredients specified under A, 0.01 gram of the supplementary dyestuff of the formula

(7)
$$H_2C_5$$

$$N-N=N-C$$

$$C-N$$

$$C=N$$

$$C_{17}H_{25}$$

Each glass plate was exposed with blue light behind a stepped wedge, developed in a Metol-hydroquinone developer to the same silver gamma ( $\gamma$ =0.56), fixed, hardened in aqueous formaldehyde solution, and dried in 75 in dilute hydrochloric acid and melting at 110° C. and

order to measure the silver image. Both plates were then treated for 30 minutes in a dyestuff bleaching bath having the following composition:

	Thioureagrams	10
•	Potassium bromidedo	12.5
	2:3-diaminophenazinedo	0.005
	Hydrochloric acid of 37% strengthcc	100
	Water to make 1 lifer.	

After being thoroughly washed with water the plates were treated for 10 minutes in a bath having the following composition:

	0.	allio
_	Potassium ferricyanide	100
b	Boric acid	8
	Sodium borate	
	Potassium bromide	50
	Water to make 1 liter.	

The plates were then washed, treated in a fixing bath, washed and dried.

Both plates had at the parts originally free from silver, when viewed through a green filter, the same maximum color density of 1.04 and they had the same densities in other parts of the spectrum. This shows that the supplementary dyestuff had been completely destroyed. Measurement of the plate A behind a green filter gave a color gamma of 1.55, whereas similar measurement of the plate B gave a color gamma of 0.70.

The dyestuff of the Formula 6 can be prepared as follows:

165 parts of 1-benzyl-1:1-di-(3'-methyl-4'-aminophenyl)-ethane are tetrazotized in the usual manner in a solution rendered acid with hydrochloric acid, and coupled with 480 parts of 1-(3'-acetylaminobenzoylamino)-8-hydroxynaphthalene-3:6-disulfonic acid in a solution rendered alkaline with sodium carbonate. The resulting purple dyestuff is filtered off and purified in the usual manner. In the form of the free acid it corresponds to the above Formula 6. It is easily soluble in water, does not diffuse in gelatine, has a high luminosity, has a good compatibility with silver halide emulsions, can be bleached to pure white, and has a good fastness to light.

The 1 - benzyl-1:1-di-(3'-methyl-4'-aminophenyl)-ethane used as starting material can be prepared as follows:

A mixture of 320 parts of 1-amino-2-methylbenzene, 300 parts by volume of concentrated hydrochloric acid and 134 parts of phenyl-acetone is stirred, and the tem-

HN-OC-CH<sub>3</sub>

perature of the mixture is raised from 60° C. to 110° C. in the course of 4 hours. Distillation is then brought about by raising the temperature to 140° C., during which water and oil are collected in a receiver. The oil is separated and returned to the reaction vessel. The mixture is stirred under reflux for about 8 hours longer at 140° C. The mixture is then taken up in water, rendered strongly alkaline with sodium hydroxide solution, and the precipitated oil is subjected to steam distillation in order to recover the excess of 1-amino-2-methylbenzene. The greasy residue remaining in the distillation vessel is dried and recrystallized from cyclohexane. There are obtained about 106 parts of colorless crystals soluble in dilute hydrochloric acid and melting at 110° C. and

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of which the properties and analysis are in conformity with the formula

(8)  $H_3C$   $CH_3$   $CH_3$   $CH_4$   $CH_2$   $CH_3$ 

The acetyl-compound of this diamine melts at 237° C. The dyestuff of the Formula 7 can be obtained by coupling diazotized 1-amino-4-diethylaminobenzene with 1-phenyl-3-heptadecyl-5-pyrazolone-4'-sulfonic acid.

### Example 2

A. Upon a glass plate there was cast a silver bromide emulsion containing the dyestuff of the formula

(15) 
$$\begin{array}{c} \mathbf{g} \\ \mathbf{H0} \\ -\mathbf{N} = \mathbf{N} - \mathbf{C} \\ \mathbf{C} = \mathbf{N} \\ \mathbf{H000C} \end{array}$$

$$15 \quad \text{HO}_{3}\text{S} - \underbrace{\begin{array}{c} \text{OH} \\ \text{HO} \\ \text{N-C} \\ \text{C-N-N-C} \\ \text{CH}_{3} \\ \text{HOOC} \\ \end{array}}_{\text{CH}_{3}} \quad \text{HO}_{3}$$

and anhydrobiguanido-benzyl alcohol acetate.

B. Upon other glass plates there were cast emulsions which contained the constituents mentioned under A and also 20 to 50% (calculated on the quantity of dyestuff of the Formula 9) of the dyestuff of the Formula 7 or one of the dyestuffs of the following formulae:

(10) 
$$H_5C_2$$
  $H_3C_3$   $H_3C_4$   $H_3C_4$   $H_3C_4$   $H_3C_5$   $H_3$   $H_$ 

(12) 
$$\begin{array}{c} \text{Ho} \\ \text{So}_3 \text{H} \\ \text{C-N-} \\ \text{C-N-} \\ \text{C-N-} \\ \text{C-N-} \\ \text{H}_4 \text{C} \end{array}$$

(13) 
$$\begin{array}{c} HO \\ C-N- \\ -N=N-C \\ C=N \\ HOOC \end{array}$$

(14) 
$$\begin{array}{c} HO \\ \hline \\ N=N-C \\ \hline \\ C=N \\ \hline \\ H_3C \\ \end{array}$$

HN-OC-C<sub>11</sub>H<sub>23</sub>

All the plates were developed, fixed, hardened and treated in a dyestuff bleaching bath as described in Example 1. The silver was then bleached out in 10 minutes in a bath which contained, per liter of water, 30 grams of potassium ferricyanide, 10 grams of potassium bromide and 10 grams of anhydrous sodium carbonate. During these treatments each of the supplementary dyestuffs of the Formulae 7 and 10 to 17 were destroyed. The plates were then fixed, washed and dried. All the layers having dyestuffs referred to under B had a flatter color gradation curve than the layer produced as described under A without such a dyestuff.

### Example 3

Upon a cellulose acetate film the following layers were cast one upon another in the order given.

(a) A red sensitized silver bromide emulsion containing copper phthalocyanine di- or tetra-sulfonic acid as a cyan dyestuff.

(b) A green sensitized silver bromide emulsion containing the purple dyestuff of the formula

70 and anhydrobiguanido-benzyl alcohol acetate.

(c) A filter layer composed of colloidal silver.

(d) A non-sensitized silver bromide emulsion having the composition given under A in Example 2.

The photographic material so produced was processed 75 by one of the usual methods of carrying out the silver

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dyestuff bleaching process, a potassium ferricyanide bath being used as the silver bleaching bath.

By incorporating the supplementary dyestuff of the Formula 7 given in Example 1 in at least one of the three layers (a), (b) and (d) the color gradation produced in the layer or layers so modified was flatter, and the color gradation in the other layer or layers was substantially unaffected.

What is claimed is:

1. In a process for the production of color photographic 10 images by the silver dyestuff bleaching method, the step which comprises decreasing the contrast obtained by bleaching at least one of the dyestuffs serving for image formation by means of a supplementary dyestuff which corresponds to the fomula

$$R-N=N-Py$$

in which R represents a member selected from the group consisting of a benzene radical, a naphthalene radical and a pyrazolone radical containing in one of the posi- 20 tions 1 and 4 relatively to the azo group a substituent selected from the group consisting of a hydroxy group and an amino group, and Py represents the radical of a 5pyrazolone bound in 4-position to the azo linkage, and by destroying completely said supplementary dyestuff in 25 an oxidizing bath following the bleaching bath.

2. A bleachable photographic silver halide emulsion layer for the silver dystuff bleaching method which contains in addition to at least one dyestuff serving for image formation, at the most an equal quantity of at least one 30 supplementary dyestuff of the formula

$$R_1$$
— $N$ — $Py$ 

in which R<sub>1</sub> represents a benzene radical which contains a hydroxyl group in para-position to the azo linkage and 35 Py represents the radical of a 5-pyrazolone bound in 4position to the azo linkage.

3. A bleachable photographic silver halide emulsion layer for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image 40 formation, at the most an equal quantity of at least one supplementary dyestuff of the formula

$$R_1$$
— $N$ — $N$ — $Py$ 

in which R<sub>1</sub> represents a benzene radical which contains 45 a hydroxyl group in para-position to the azo linkage and Py represents the radical of a 1-phenyl-5-pyrazolone containing a sulfonic acid group in the phenyl radical and bound in 4-position to the azo linkage.

er for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image

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formation, at the most an equal quantity of at least one supplementary dyestuff of the formula

$$R_1$$
— $N$ — $N$ — $Py$ 

in which R<sub>1</sub> and Py each represents the radical of a 1phenyl-5-pyrazolone bound in 4-position to the azo linkage, at least one of the phenyl radicals containing a sulfonic acid group.

5. A bleachable photographic silver halide emulsion layer for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image formation, at the most an equal quantity of the supplementary dyestuff of the formula

$$\begin{array}{c} \text{Ho} \\ \text{C-N-} \\ \text{N-} \\ \text{H_5C_2} \\ \text{N-} \\ \text$$

6. A bleachable photographic silver halide embulsion layer for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image formation, at the most an equal quantity of the supplementary dyestuff of the formula

$$\begin{array}{c} \text{HO} \\ \text{N=N-C} \\ \text{C=N} \\ \text{H2C} \end{array}$$

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