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PHOTOGRAPHIC LAYERS

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16 Claims. (Cl. 96—99)

This is a continuation-in-part of my copending patent application Ser. No. 93,835, filed March 7, 1961, now abandoned.

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 azo-dyestuffs 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 the silver image.

The method can be applied to a colored layer produced by coloring the layer-forming substance with the azo-dyestuff before the layer is formed or by coloring the finished layer on its support. The method can also be applied to multilayer 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 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 incadescent 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 contains 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 2-amino-3-hydroxyphenazine, 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 practically colorless decomposition products according to the following equation:

$$R_1—N{=}N—R_2 + 4Ag + 4HBr \rightarrow R_1—NH_2 + H_2N—R_2 + 4AgBr$$

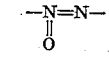
R_1 represents the radical of the diazo-compound obtainable from the diazo-component $R_1—NH_2$ and R_2 represents the radical of the coupling component $H—R_2$. By the splitting reaction the diazo-component is regenerated, and an amino-compound $H_2N—R_2$, is formed from the radical of the coupling components. In the case of disazo- or polyazo-dyestuffs there are also obtained as fission products diamines, for example:

$$R_2—N{=}N—R_3—N{=}N—R_2 \rightarrow 2R_2—NH_2 + H_2N—R_3—NH_2$$

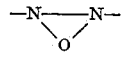
Unconsumed image silver is removed in known manner, for example, with Farmer's reducer, and also the silver

bromide formed in the bleaching process. In this manner a positive copy of the originial is obtained.

The present invention is based on the observation that it is advantageous to use azoxy-dyestuffs, instead of or in addition to azo-dyestuffs, in photographic layers to be used for the silver dyestuff bleaching method. Accordingly, the present invention provides photographic silver halide gelatine layers suitable for the silver dyestuff bleaching method, containing as image dyestuffs dyestuffs that contain at least one azoxy group. For the azoxy group there is used herein the formula



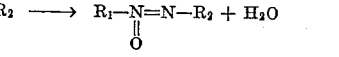
which reflects reality better than the formula



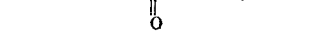
which contains two trivalent ntirogen atoms.

With azoxy-dyestuffs yellow, red, purple, blue and green-blue tints are produced not only on textiles, as is known, but also in photographic layer, especially those of gelatine. The azoxy dyestuffs preferably contain at least one group imparting solubility in water.

The preparation of azoxy-dyestuffs is adequately described in the literature. They are obtained, for example, by condensing nitro compounds with amines as follows:



or by the reduction of nitro-compounds under very special conditions as follows:



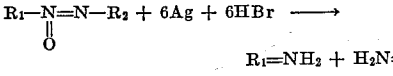
In the latter case the reduction is generally carried out with the use of arseneous acid or with the use of glucose in an alkaline medium.

In this manner azoxy-polyazo-dyestuffs can also be obtained, that is to say dyestuffs which contain, for example, one azoxy group and at least two azo groups. These dyestuffs produce blue tints. There are also known azoxy-polyazo-dyestuffs which contain groups capable of forming metal complexes and are, therefore, capable of forming complex heavy metal compounds. Such azo-azoxy-dyestuffs capable of forming metal complexes, and azoxy-dyestuffs free from azo groups and which are capable of forming metal complexes, may contain as the complex-forming group, for example, a salicylic acid radical, and may be used in the non-metallized condition to produce the colored layers, and converted, after the silver dyestuff bleaching operation, into the complex heavy metal compounds, for example, by means of a solution of copper acetate or another agent yielding metal.

Instead of converting the dyestuffs subsequently into their complex metal compounds, photographic materials may be colored with the pre-formed complex metal compounds prepared in substance, for example, silver halide emulsions so colored may be used for casting.

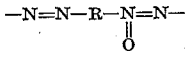
The complex metal compounds, and especially the complex copper compounds, whether prepared in substance or produced in the colored layer, are distinguished by their very good fastness to light. They can be bleached out completely by the silver dyestuff bleaching method at the areas having the highest density of silver, and this could not be foreseen. It is necessary to take into account the fact that the complex metal compounds of metals having atomic numbers from 22 to 29, and especially the complex copper compounds yield deeper tints than do the

metal-free dyestuffs. The azoxy group undergoes reduction in accordance with the following equation



so that a larger quantity of image silver is required to bring about the reduction than in the case of the azo group. This greater consumption of image silver, as compared with the consumption required for reducing the azo group, leads to relatively flat color gradations, which are very desirable for certain copying processes.

For the purposes of this invention it is of advantage to use azoxy-dyestuffs which are homogeneous compounds and contain a definite small number, for example, one or two azoxy groups in the molecule. They may contain, for example, an atomic grouping of the formula

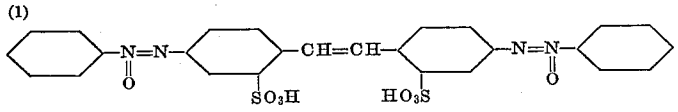


in which R represnts a benzene or naphthalene nucleus, which contains in a position vicinal to the azo group a substitutent capable of taking part in the formation of heavy metal complexes, for example, a carboxylic acid, carboxy-methoxy, methoxy or hydroxyl group.

There are given below a few dyestuffs suitable for the purposes of the invention.

No. 1 The yellow dyestuff of the formula

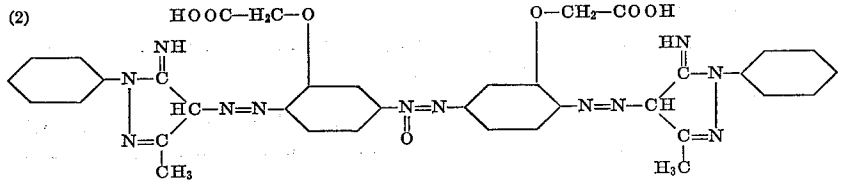
(1)



which is obtainable by condensing 4:4'-dinitro-stilbene disulfonic acid with aniline in the molecular ration 1:2.

No. 2 The red dyestuff of the formula

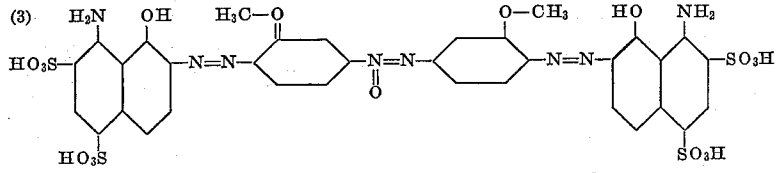
(2)



This dyestuff dyes gelatine yellowish-red and can be converted into its complex copper compound, which is very fast to light and yields bluish-red tints.

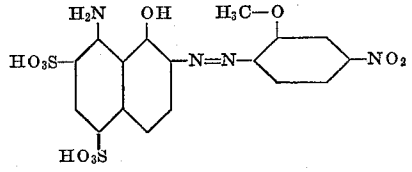
No. 3 The blue dyestuff of the formula

(3)



which is obtainable from the nitro-monoazo-dyestuff of the formula

3a)



by reduction with the aid of heat with glucose in a solution rendered alkaline with an alkali metal hydroxide.

This azoxy-disazo dyestuff yields a blue tint having an absorption maximum at 620° mμ. The fastness to light of the blue color image produced by the silver dyestuff bleaching process with this dyestuff can be considerably improved by treating with a solution of 2 to 5% strength of an agent yielding copper, such as sodium copper tartrate.

This dyestuff itself possesses a remarkably low capacity for diffusion so that it has hardly any tendency to migrate into an adjacent layer. However, the resistance to diffusion in gelatine can be still further improved by suitable additions, for example, a guanidine base.

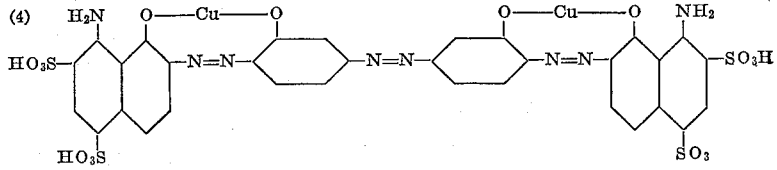
In general azoxy dyestuffs having a good resistance to diffusion can be produced by incorporating into the molecule of the dyestuff a radical which imparts resistance to diffusion. Thus, in the aforesaid dyestuff No. 3 the primary amino group may be replaced by groups of the formula

in which R_4 represents a hydrogen atom or an alkyl group, and R_5 represents an acyl, sulfacyl or aracyl group or the chain of an aliphatic or hydro-aromatic radical. Thus, for example, R_5 may represent a benzyl radical, for example, a dichlorobenzyl radical, a benzoyl radical, a dichlorobenzoyl radical, a para-toluene-sulfonyl radical, or an aliphatic hydrocarbon radical, which may be interrupted by hetero atoms, such as an amyl, n-octadecyl, n-octadecenyl, dodecyl-hydroxypropyl or stearoyl radical.

Furthermore, there may be used, instead of the dyestuff No. 3 or another azoxy-dyestuff, containing ortho-hydroxy-ortho'-methoxy-azo groupings, the corresponding ortho:ortho'-dihydroxyazo-metal complex compound obtainable in substance by metallization accompanied by demethylation. From dyestuff No. 3 the following dyestuff can be obtained in this manner.

No. 4. The tint of this dyestuff is changed considerably towards green-blue as compared with the tint of dyestuff No. 3. Dyestuff No. 4 corresponds to the formula

(4)

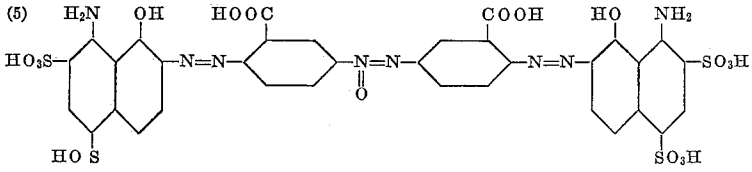


its absorption maximum in gelatine is at about 670 mμ. It can also be completely bleached out well by the silver

dyestuff bleaching method at the areas having the maximum density of silver, and it has an excellent fastness to light. The bleaching out of this dyestuff can be still further improved by extracting the dyestuff at the boil with hydrochloric acid or a cyanide to remove the copper bound in complex union, and, after the bleaching operation reintroducing the copper into the metal-free dyestuff by treatment with a bath containing a water-soluble copper compound.

No. 5. The blue dyestuff of the formula

(5)

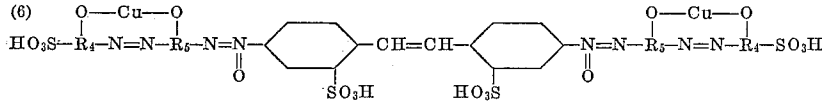


This dyestuff gelatine blue and is bleached out completely by the usual silver dyestuff bleaching baths at the areas of maximum density of silver. The above remarks with regard to metallization in connection with dyestuffs Nos. 3 and 4 also apply to this dyestuff.

In addition to the azoxy-dyestuffs listed under (1) to (5) above, those described hereinafter under A, B and C are particularly valuable as image dyestuffs in the silver dyestuff bleaching method.

A. The azoxy dyestuffs of the formula

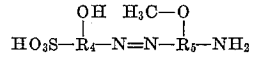
(6)



wherein R_4 and R_5 each represent a moncyclic benzene radical bound in ortho-position to the azo group and the —O—Cu—O-group, the azo and azoxy groups being bound in para-position to the benzene radicals R_5.

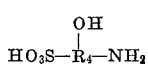
The azoxy dyestuffs of Formula 6, some of which are known, are obtained by condensing 4:4'-dinitrostilbene-2:2'-disulfonic acid in a molecular ratio of 1:2 with aminoazo dyestuffs of the formula

(7)



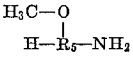
in which R_4 and R_5 have the meaning given above and then metallizing with an agent yielding copper accompanied by demethylation of the methoxy groups. The aminoazo dyestuffs are obtained by coupling diazo compounds of orthohydroxyamines of the formula

(8)



with amines of the formula

(9)



which couple in paraposition to the amino group, wherein R_4 and R_5 have the meanings given above.

The amines of the Formula 8 may contain additional substituents, for example, halogen atoms such as chlorine, alkyl groups such as ethyl or methyl groups, nitro groups or further sulfonic acid groups. As diazo components of the kind defined there may be mentioned, for example,

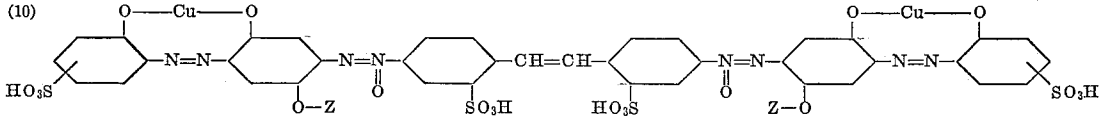
2-amino-1-hydroxy-4-chlorobenzene-6-sulfonic acid,
2-amino-1-hydroxy-5-chlorobenzene-6-sulfonic acid
2-amino-1-hydroxy-6-chlorobenzene-4-sulfonic acid,
2-amino-1-hydroxy-4-methylbenzene-6-sulfonic acid,
2-amino-1-hydroxybenzene-4:6-disulfonic acid,
2-amino-1-hydroxy-6-nitrobenzene-4-sulfonic acid and
2-amino-1-hydroxy-4-nitrobenzene-6-sulfonic acid.

The coupling components of Formula 9 may also contain further substitutents, for example, a methyl group in para-position to the methoxy group, but more especially an ethoxy group or a methoxy group in the said position. As examples there may be mentioned:

1-amino-3-methoxybenzene,
1-amino-2-methyl-5-methoxybenzene,
1-amino-2-ethoxy-5-methoxybenzene and
1-amino-2:5-dimethoxybenzene.

Specially good results are generally obtained with azoxy dyestuffs of the formula

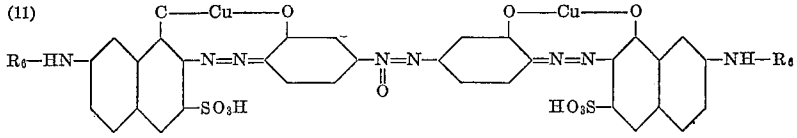
(10)



in which Z represents an alkyl group containing at most 2 carbon atoms.

B. The azoxy dyestuff of the formula

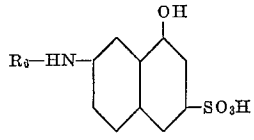
(11)



in which R_6 represents a monocyclic benzene radical.

The azoxy dyestuff of Formula 11, some of which are known, are obtained by coupling diazotized 5-nitro-2-amino-1-hydroxybenzene in an alkaline medium with a 2-phenylamino-8-hydroxynaphthalene-6-sulfonic acid of the formula

(12)



in which R_6 has the meaning given above, condensing the nitroazo dyestuff with the formation of an azoxy group from two nitro groups and then coppering. The 2-phenylamino-8-hydroxynaphthalene-6-sulfonic acids used as coupling components in this process may contain further substituents in the phenyl radical, for example, halogen atoms, for example, chlorine, alkyl groups, for example, a methyl group, alkoxy groups, for example, a methoxy group, acidic groups imparting solubility in water, for example, carboxylic acid groups, carboxy-

methoxy groups (HOOC—CH_2—O—) or especially sulfonic acid groups. As examples there may be mentioned:

2-phenylamino-8-hydroxynaphthalene-6-sulfonic acid-4'-carboxylic acid,
2-phenylamino-8-hydroxynaphthalene-6:3'-disulfonic acid and
2-phenylamino-8-hydroxynaphthalene-6-sulfonic acid.

The photographic layers that contain azoxy dyestuffs of the formulae 6 or 11 can be of the usual composition and can be prepared in known manner. The supports for the silver halide layers can be, for example, glass for duplicate positives, or they can be made of cellulose esters, or they can be opaque, white-pigmented films, baryta paper or reflecting supports.

In the conventional silver dyestuff bleaching process a positive copy is obtained by copying a transparent, colored master image on a dyed gelatine layer containing silver halide. By using, in the silver dyestuff bleaching process, copying material dyed black with transparent dyestuffs, positive (rectified) copies are obtained in a simple manner from a black and white original. When a colored positive master image is copied on such a silver halide layer dyed a transparent black that, if necessary, may be sensitized to the color concerned, a positive black and white copy of the colored original is obtained, the grey tones being graduated. The azoxy dyestuffs of Formulae 6 and 11 are specially suitable for the production of such copies.

The black dyestuffs used in the silver dyestuffs bleaching process must possess a wide range of properties. A high degree of light fastness is required and the dyestuffs should be capable of being bleached to neutral grey tones. They must be non-diffusing or must be capable of being rendered non-diffusing with precipitating agents, for example, guanidines. The dyestuffs of Formulae 6 and 11 meet these requirements to a large extent.

Very strong acid baths are used in the course of the bleaching process which means that the copper-containing dyestuffs are partially demetallized. It is, therefore, of advantage to treat the dyestuffs with a copper-yielding agent in a slightly acid to alkaline medium at the end of the bleaching process in order to convert the demetallized portion back to the complex copper compound.

C. The azoxy dyestuffs of the formula

(13) $R_8—N=N—R_7—\underset{\underset{O}{\|}}{N}=N—R_7—N=N—R_8'$

wherein R_7 represents a monocyclic benzene ring bound to the azo group in 1-position and to the azoxy group in 4-position and containing in 2-position a substituent selected from the group consisting of an alkoxy group and a hydroxyalkoxy group containing at most 5 carbon atoms, and R_8 and R_8' each represents the radical of an 8-hydroxy-naphthalene-disulfonic acid bound to the azo group in its 7-position and containing in its 1-position a further substituted amino group.

The dyestuffs of Formula 13 may be prepared by treating a nitromonoazo dyestuff of the formula

(14) $R_8—N=N—R_7—NO_2$

in which R_7 represents a benzene radical bound in the 1-position to the azo group and in the 4-position to the nitro group and containing in the 2-position an alkoxy group or a hydroxyalkoxy group with at most 5 carbon atoms, and R_8 has the meaning given above, with a reducing agent which is capable of reducing a nitro compound to an azoxy compound with the linking of two molecules. This method is particularly suitable for the

preparation of symmetrical compounds of the Formula 13($R_8=R_8'$).

Unitary asymmetrical as well as symmetrical dyestuffs of the Formula 13 may be prepared by coupling a tetrazo compound of a diamine of the formula

(15) $H_2N—R_7—\underset{\underset{O}{\|}}{N}=N—R_7—NH_2$

on either side with one of two different aminohydroxynaphthalenedisulfonic acids, or on each side with an identical azo component of this kind. In the Formula 15 R_7 represents a benzene radical bound in the 1-position to the amino group and in the 4-position to the azoxy group and containing in the 2-position an alkoxy group or a hydroxyalkoxy group with at most 5 carbon atoms. The compounds of the Formula 15 may in their turn be prepared by reducing a 1-acylamino-2-alkoxy-4-nitrobenzene or a 1-acylamino-2-hydroxyalkoxy-4-nitrobenzene to form an azoxy compound of the formula

(16) Acyl-HN—R_7—$\underset{\underset{O}{\|}}{N}$=N—$R_7$—NH-Acyl

in which R_7 has the meaning given above, and by subsequent hydrolysis of the acylamino group.

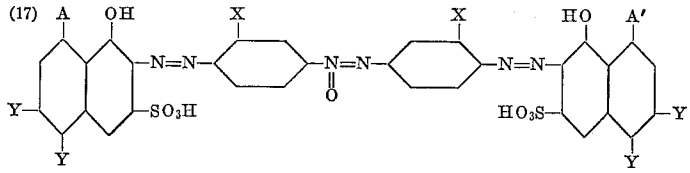
The 1-acylamino-2-alkoxy-4-nitrobenzenes or 1-acylamino-2-hydroxyalkoxy-4-nitrobenzenes used for the preparation of the diamines of the Formula 15, and the corresponding amino compounds employed for the preparation of the nitromonoazo dyestuffs of Formula 14 contain in the ortho-position to the acylamino group or to the amino group for example a methoxy, n-propoxy, isopropoxy or n-butoxy group. As a rule ethoxy and hydroxyethoxy groups are particularly advantageous. Further substituents, for example a methyl or ethyl group or a chlorine atom, may be present in these compounds but are not necessary.

The 8-hydroxynaphthalenedisulfonic acids with a further substituted amino group in the 1-position, used as azo components for the preparation of the dyestuffs of Formula 13 according to the methods shown, contain the sulfonic acid groups preferably in the 3,6- or 4,6-position. The amino group in the 1-position is further substituted, for example by alkyl groups, such as ethyl or methyl, by benzene radicals which may themselves bear further substituents, by cycloalkyl radicals such as cyclohexyl, or advantageously by acyl radicals. The acyl radicals are derived from carboxylic acids or sulfonic acids, especially those of the benzene series, in which latter case the benzene nuclei may bear further substituents, for example chlorine atoms or alkyl radicals, particularly methyl groups. The following examples may be mentioned:

1-phenylamino-8-hydroxynaphthalene-3,6-disulfonic acid,
1-phenylamino-8-hydroxynaphthalene-4,6-disulfonic acid,
1-cyclohexylamino-8-hydroxynaphthalene-3,6-disulfonic acid,
1-cyclohexylamino-8-hydroxynaphthalene-4,6-disulfonic acid,
1-benzoylamino-8-hydroxynaphthalene-3,6-disulfonic acid,
1-para-toluenesulfonylamino-8-hydroxynaphthalene-3,6-disulfonic acid,
1-para-toluenesulfonylamino-8-hydroxynaphthalene-4,6-disulfonic acid,
1-para-toluenesulfonylamino-8-hydroxynaphthalene-3,5-disulfonic acid,
1-(3'-carboxy-4'-hydroxybenzenesulfonylamino)-8-hydroxynaphthalene-3,6-disulfonic acid.

From the above it is clear that for the present invention the azoxy dyestuffs of the following formulae are especially suitable:

(17)



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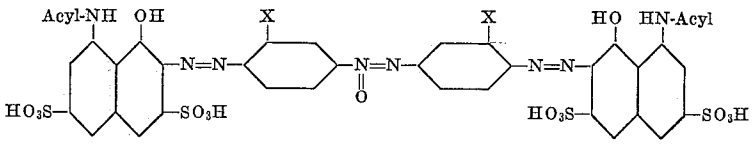

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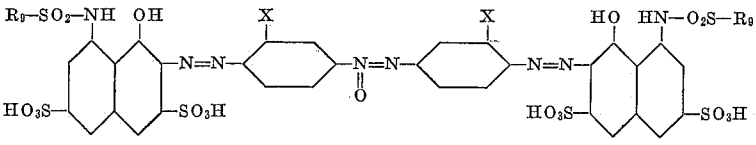


In these formulae, X represents an alkoxy or hydralkoxy group with at most 5 carbon atoms, A and A' each represents a further substituted amino group, R_9 represents a monocyclic benzene radical, and in each naphthalene radical of the Formula 17 one Y stands for a hydrogen atom and the other Y for a sulfonic acid group.

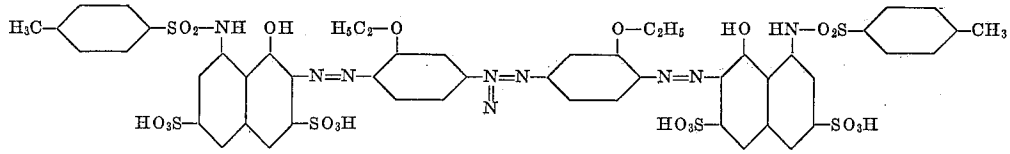
The dyestuffs of Formulae 13, 17, 18 and 19 may be prepared in a conventional manner known per se. In order that the coupling may take place in the 7-position, that is to say in vicinal position to the hydroxyl group of the hydroxynapthalene compound, the reaction is carried out in an alkaline medium. The reduction of the nitro dyestuffs to form the azoxy dyestuffs is advantageously performed with glucose in an aqueous sodium hydroxide solution.

According to the process of the invention these dyestuffs are present in photographic layers for the silver dyestuff bleaching process, These materials may be constituted and prepared in a manner known per se. The silver halide emulsion layers colored with the green-blue dyestuffs may advantageously be sensitized to red light and form a constituent of a multilayer material, suitable for the production of multicolored prints, which contains in addition to this green-blue layer at least one magenta layer sensitized to green light and a yellow layer, and may contain further layers which do not contain any image dyestuffs. The gelatine layers colored with the dyestuffs of Formula 13 show particularly pure tints and especially favorable absorption curves.

A few prescriptions for the preparation of some dyestuffs of Formula 13 are given below. In these prescriptions and in the subsequent examples the parts and percentages are by weight unless otherwise stated.

(6) 76.5 parts of the nitroazo dyestuff, obtained by coupling 1-amino-2-ethoxy-5-nitrobenzene with 1-toluenesulfonylamino-8-hydroxynaphthalene-3,6-disulfonic acid in alkaline medium, are reduced in 5 to 10 minutes at a temperature between 75 and 90° C. in 2000 parts of water and 100 parts of an aqueous sodium hydroxide solution of 40% by volume with 17 to 18 parts of glucose, dissolved in 60 parts of water. The azoxy dyestuff of the formula

(20)

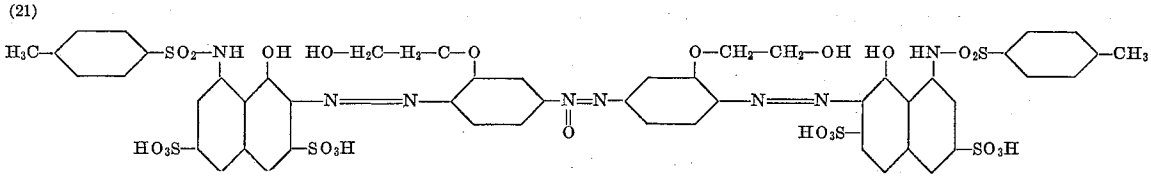


is formed in very good yield and can be separated by the addition of sodium chloride. It dissolves in water with a greenish blue shade. When the dyestuff is dissolved in gelatine, the solution shows a green-blue layer with an absorption maximum of 640 mμ.

The dyestuffs shown under (7) to (9) below may also be prepared by this method.

(7) The dyestuff of the formula

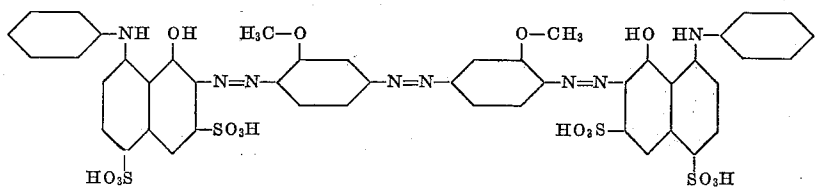
(21)



Absorption maxima in gelatine at 640 and 690 mμ.

(8) The dyestuff of the formula

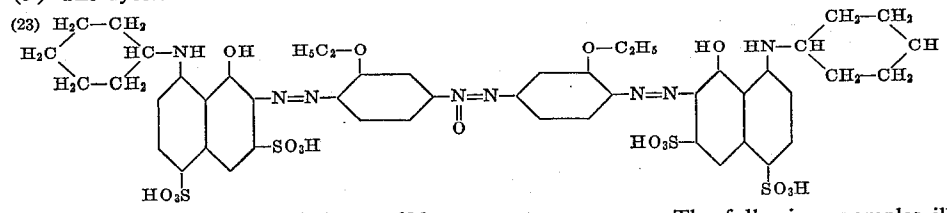
(22)



Absorption maximum in gelatine at 620 mμ.

(9) The dyestuff of the formula

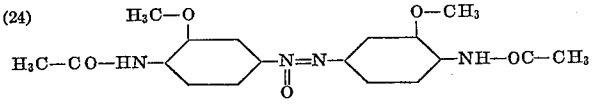
(23)



Absorption maximum in gelatine at 620 mμ.

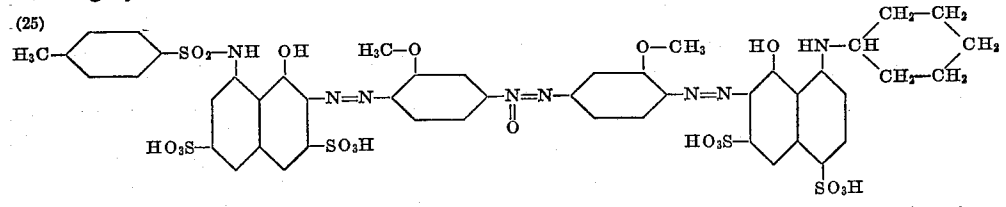
(10) 1-acetylamino-2-methoxy-4-nitrobenzine is converted at 40 to45° C. with zinc dust in ammoniacal ethanol solution into the azoxy compound of the formula

(24)



The acetylamino groups are hydrolysed. The resuting 3,3' - dimethoxy - 4,4 - diaminoazobenzene is tetrazotized and the tetrazo compound coupled on the one side with 1 - paratoluenesulfonylamino - 8 - hydroxynapthalene-3,6-disulfonic acid and on the other side with 1-cyclohexylamino-8-hydroxynapthalene-4,6-disulfonic acid. The resulting dyestuff of the formula

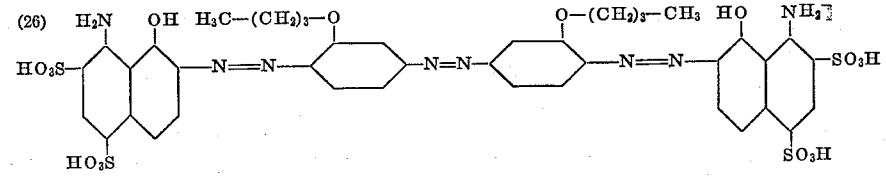
(25)



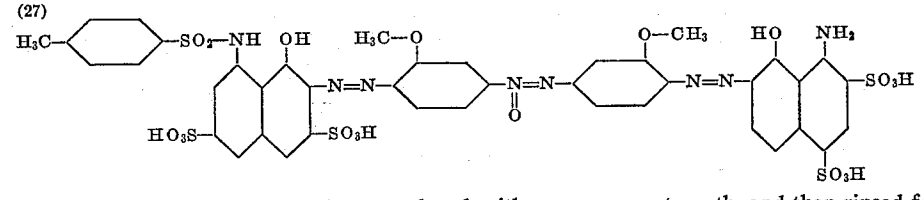
colours gelatine green-blue shades.

Moreover the following dyestuffs which are similar in constitution to those of Formula 13 and can be prepared in analogous manner may be used in accordance with this invention:

(26)



(27)



When it is desired to use layers colored with azoxy-dyestuffs to produce matrices for an imbibition process, dyestuffs that diffuse well are desired. On the other hand, when the silver dyestuff bleaching method is used for the production of multi-color pictures a three-layer material is required, in which the several dyestuffs are as resistant as possible to diffusion and are yet water-soluable. The water-solubility is imparted by the usual groups imparting solubility in water, advantageously sulfonic acid and/or carboxylic acid groups. A good resistance to diffusion can be imparted by introducing the substituents mentioned above in connection with dyestuff No. 3 or by converting the too easily diffusible dyestuff acid or akali metal salt into a non-diffusing salt, for example, with an organic base or a biguanide. These expedients may of course be used in combination.

The azoxy-dyestuffs can also be used for incorporation in so-called droplet-emulsions ("packed emulsions") or for mixed grain emulsion systems.

The following examples illustrate the invention.

Example 1

6 grams of dyestuff No. 3 (see above) are dissolved in 550 cc. of water, the solution is mixed with a red sensitized silver bromide gelatine emulsion, and the homogenized mixture is cast as a layer on a suitable support, for example, an acetyl-cellulose film having a substream layer, so that the dry layer contains 15 milligrams of silver in the form of silver bromide and 7 milligrams of dyestuff per square decimeter.

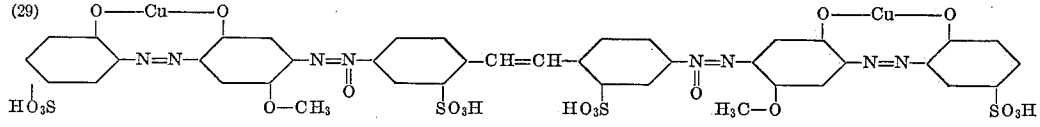
The resulting blue layer can be used as such or it may be used as part of a three-layer material. The layer is exposed behind a colored diapositive or beneath a positive component color image to red light. The exposed layer is developed with a developer containing 0.75 gram of N-methyl-para-aminophenol, 3 grams of hydroquinone, 25 grams of sodium sulfite, 40 grams of anhydrous sodium carbonate and one gram of potassium bromide per liter of water. The layer is then rinsed for one minute in water, fixed with sodium thiosulfate solution of 20% strength, and then rinsed for one minute with water. The layer is advantageously hardened with formaldehyde solution of 4% strength, and then washed. The silver bleaching bath contains, for example, 100 cc. of hydrochloric acid having a density of 1.19, 12.5 grams of potassium bromide and 10 grams of thiourea dissolved in one liter of water, and if desired, 0.1 gram of dimethylquinoxaline. The bleaching process takes 8 to 15 minutes, and then the layer is washed for five minutes. The layer is then treated in a silver bleaching bath to convert the silver into silver halide. This bath contains, for example, 100 grams of crystalline copper sulfate, 100 grams of sodium-chloride and 50 cc. of hydrochloric acid (density=1.19) in one liter of water. The treatment in this bath lasts 3 to 8 minutes. The layer is then washed for five minutes and fixed for 3 to 5 minutes in a bath containing 200 grams of sodium thiosulfate in one liter of water. The layer is finally washed for 10 minutes. In order to increase the fastness to light of the dyestuff the layer is after-

treated with a copper acetate solution of 2.5% strength for 10 minutes, and is then washed for one minute. There is obtained a blue component color image of very good fastness to light.

Example 2

15 grams of dyestuff No. 2 are dissolved in the form of the non-coppered sodium salt in 1000 cc. of water at 80° C. The solution is rapidly cooled to 40° C., and mixed with 1000 grams of a gelatine solution of 10%

(29)



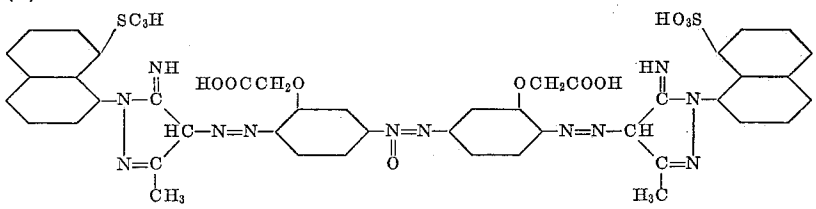
strength having a temperature of 40° C., and the whole is stirred for a short time. The colored gelatine is then mixed with 1000 grams of a silver bromide gelatine emulsion, which may be yellow-green sensitized and contains a quantity of silver bromide such that, after being cast and dried the layer contains 15 milligrams of silver per square decimeter. The layer so produced can be used as such or as one of the layers of a three-color material. After being exposed the layer is treated as follows:

(1) A silver image is developed for 8 minutes at 20° C. with a bath which contains dissolved in 1000 cc. of water 0.75 gram of N-methyl-para-amino-phenol, 3 grams of hydroquinone, 25 grams of sodium sulfite, 40 grams of sodium carbonate and 1 gram of potassium bromide;
(2) Washed for three minutes;
(3) Fixed for 5 minutes in a solution containing 200 grams of sodium thiosulfate and 20 grams of potassium meta-bisulfite per liter of water;
(4) Washed for 5 minutes;
(5) Hardened for 5 minutes with an aqueous solution of formaldehyde of 4% strength;
(6) Washed for 5 minutes;
(7) The dyestuff image is bleached for 10 to 30 minutes with a solution containing, per liter of water, 60 to 100 grams of postassium bromide, 40 to 75 grams of thiourea, 35 to 80 grams of hydrochloric acid of 30% strength and 0.001 gram of amino-hydroxyphenazine;
(8) Washed for 10 minutes;
(9.) The residual silver is bleached for 10 minutes and the dyestuff is simultaneously converted into its copper compound by means of a solution of 60 grams of copper sulfate, 80 grams of potassium bromide and 10 cc. of glacial actic acid per liter of water; (the yellowish-red tint changes towards blue-red, especially markedly after bath No. 10);
(10) Washed for 5 minutes;
(11) Fixed for 5 minutes as described in 3 above; and
(12) Washed for 10 minutes.

After being dried, the layer has a bluish red image of good fastness to light.

By using instead of the aforesaid dyestuff No. 2, the dyestuff of the formula

(28)



there is obtained a blue-red image having a somewhat purer tint and which is fast to light.

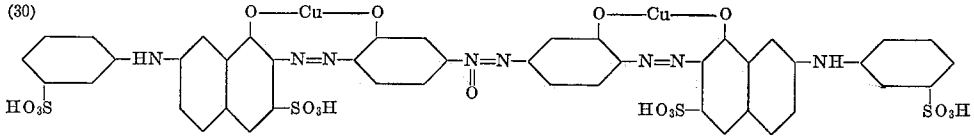
By using in this example, instead of the aforesaid dyestuff No. 2 the same quantity of the yellow dyestuff No. 1 and otherwise following the same procedure, a yellow component image is obtained.

Example 3

2 parts of one of the salt-free cupriferous dyestuffs of the formulae

or

(30)



are dissolved in 100 parts of water at 40° C., and the solution is mixed with a preparation obtained by allowing 15 to 30 parts of gelatine to swell in 300 to 600 parts and then melting the gelatine at 40° C. The amount of gelatine used depends on the support on which the prepared emulsion is to be cast. 300 to 600 parts of a silver bromide emulsion that can be orthochromatically or panchromatically sensitized are added to the colored gelatine. Furthermore, water to reduce the viscosity, aqueous solutions of spreading and dispersing agents, for example, saponin, and/or aqueous solutions of hardening agents can be added to the mixture.

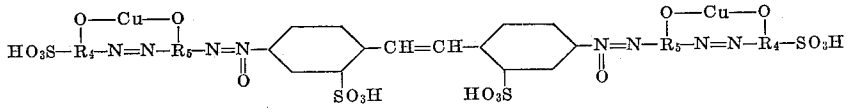
10 cc. of an emulsion so prepared are cast on a glass plate measuring 13 x 18 cm. and dried. The layer is exposed beneath a black and white positive image and the silver image developed in a bath which contained in 1000 parts of water, 80 parts of anhydrous sodium sulfite, 55 parts of anhydrous sodium carbonate, 20 parts of sodium borate and 8 parts of N-methyl-para-aminophenol sulfate. Development takes 4 to 6 minutes. The layer is given a short wash with water and then fixed for 5 minutes in a bath which contains 200 parts of sodium thiosulfate dissolved in 1000 parts of water. The layer is again washed for 5 minutes.

The layer is then bleached for 2 to 5 minutes in a bath which contains 60 parts of 32% hydrochloric acid, 10 parts of potassium bromide, 6 parts of thiourea and 0.001 to 0.002 part of a-amino-3-hydroxyphenazine dissolved in 1000 parts of water. It is then washed with water for 5 minutes, and the unconsumed image silver converted into silver bromide by a treatment for 3 to 5 minutes in a bath which contains 60 parts of crystalline copper sulfate, 60 parts of potassium bromide and 20 parts of 32% hydrochloric acid in 1000 parts of water.

After a short wash with water, the layer is fixed for 5 minutes in a bath which contains 100 parts of sodium thiosulfate in 1000 parts of water, and again washed. The image is then treated for 5 minutes in a bath which contains 25 parts of copper sulfate in 1000 parts of water. The layer is then given a final wash for 3 to 5 minutes.

A positive black and white image is obtained which is a duplicate of the original having fine, neutral grey intermediate tones. This image is distinguished by a high de-

gree of transparency of the grey gradations and by freedom from grain. By using a panchromatically sensitized emulsion positive copies in black and white can be obtained from a positive color transparency.

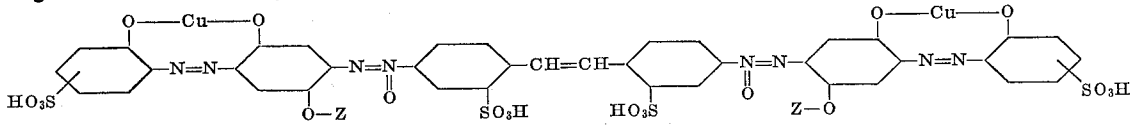


Example 4

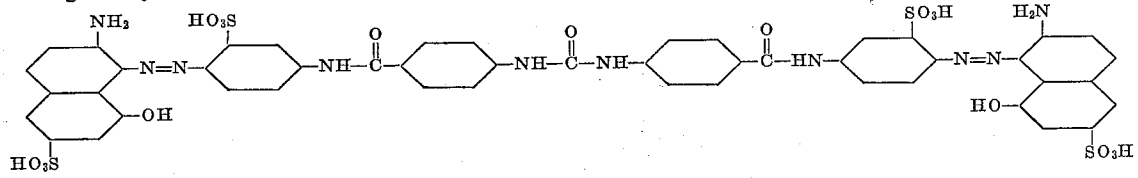
The following layers are poured on top of each other, in the sequence shown, on to a white pigmented cellulose acetate film:

(1) A red sensitized silver bromide emulsion containing the green-blue dyestuff of Formula 20.

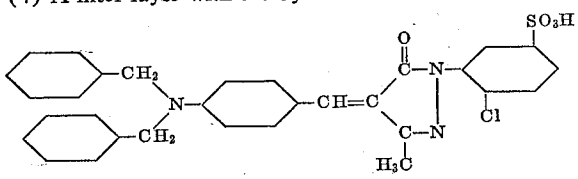
(2) A thin gelatine intermediate layer.



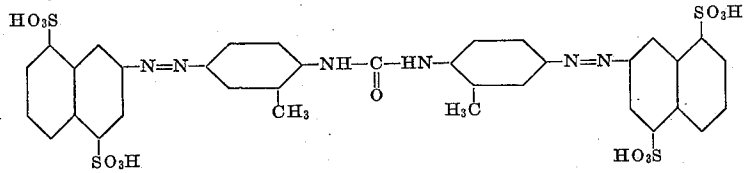
(3) A green sensitized silver bromide emulsion with the magenta dyestuff of the formula



(4) A filter layer with the dyestuff of the formula



(5) An unsensitized silver bromide emulsion with the dyestuff of the formula



The material is exposed, fixed and hardened, then bleached in a dyestuff bleaching bath containing hydrochloric acid, potassium bromide, thiourea and 2-amino-3-hydroxyphenazine, and finally freed from excess silver. An image corresponding to the copy is obtained. The dyestuff of Formula 20 is found to be fast to diffusion, bleached pure white at the areas of maximum density of silver and shows a good fastness to light.

Similar results can be obtained with the dyestuffs of Formulae 21, 22, 23, 25, 26 and 27 instead of with the dyestuff of Formula 20.

What is claimed is:

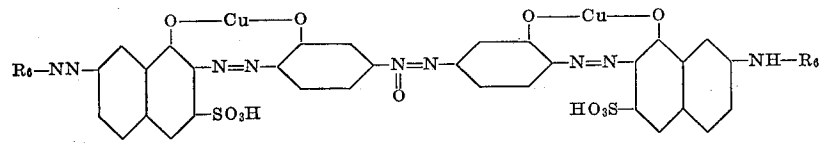
1. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula

wherein R_4 and R_5 each represent a monocyclic benzene radical bound in ortho-position to the azo group and the —O—Cu—O-group, the azo and azoxy-groups being bound in para-position to the benzene radicals R_5.

2. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula

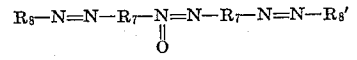
wherein Z represents an alkyl group having at most 2 carbon atoms.

3. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula



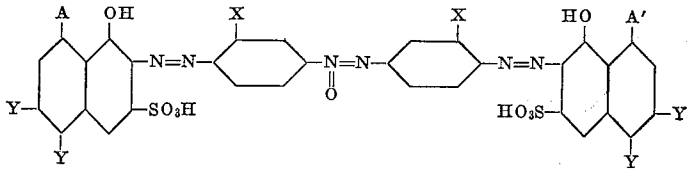
wherein R_6 represents a monocyclic benzene radical.

4. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an ozoxy dyestuff of the formula



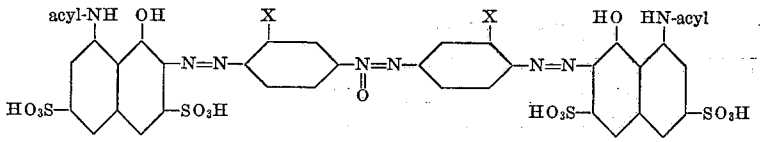
wherein R_7 represents a monocyclic benzene ring bound to the azo group in 1-position and to the azoxy group in 4-position and containing in 2-position a substituent selected from the group consisting of an alkoxy group and a hydroxy-alkoxy group containing at most 5 carbon atoms, and R_8 and R_8' each represent the radical of an 8-hydroxynaphthalene-disulfonic acid bound to the azo group in its 7-position and containing in its 1-position a member selected from the group consisting of a phenylamino group, a cyclohexylamino group, a benzoylamino group, a para-toluenesulfonylamino group and a 1-(3'-carboxy-4'hydroxybenzenesulfonylamino) group.

5. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula



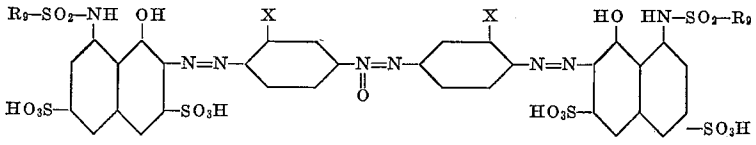
wherein A and A' each represents a member selected from the group consisting of a phenylamino group, a cyclohexylamino group, a benzoylamino group, a para-toluenesulfonylamino group and a 1-(3'-carboxyl-4'hydroxybenzenesulfonylamino) group, X represents a member selected from the group consisting of an alkoxy group and a hydroxyalkoxy group containing at most 5 carbon atoms, and in each naphthalene radical one Y represents a hydrogen atom and the other Y represents a sulfonic acid group.

6. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula



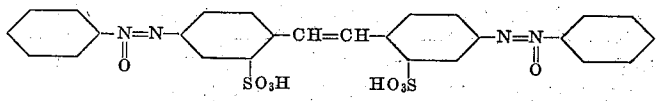
wherein X represents a member selected from the group consisting of an alkoxy group and a hydroxyalkoxy group containing at most 5 carbon atoms.

7. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff an azoxy dyestuff of the formula

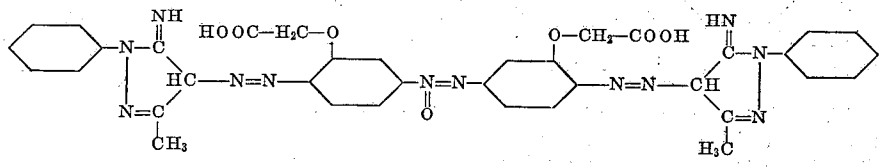


wherein X represents a member selected from the group consisting of an alkoxy group and a hydroxyalkoxy group containing at most 5 carbon atoms and R_9 represents a monocyclic benzene radical.

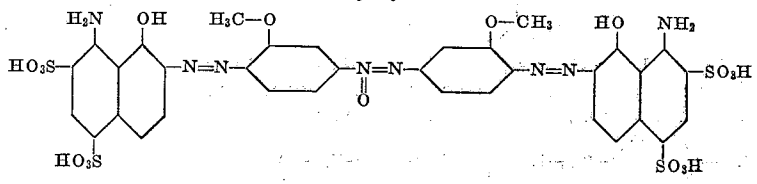
8. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



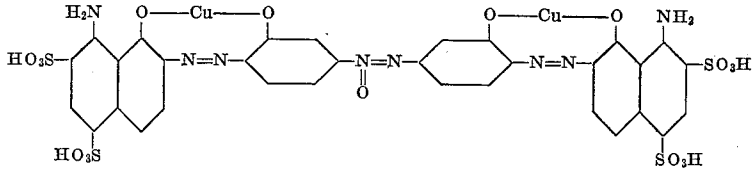
9. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



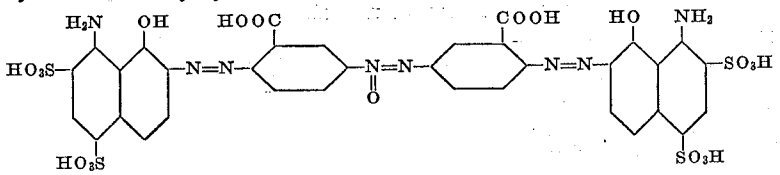
10. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



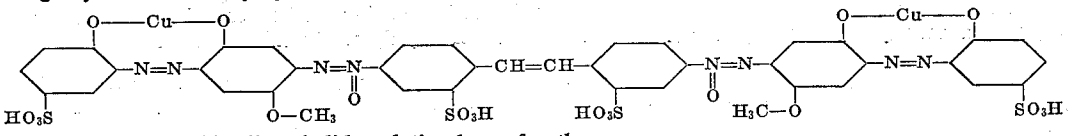
11. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



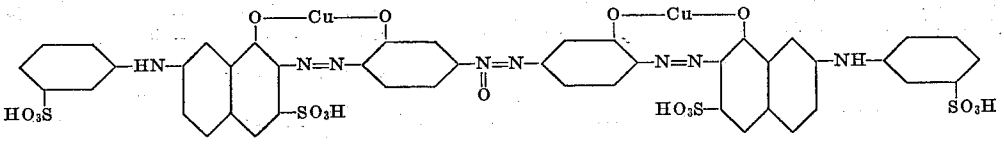
12. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



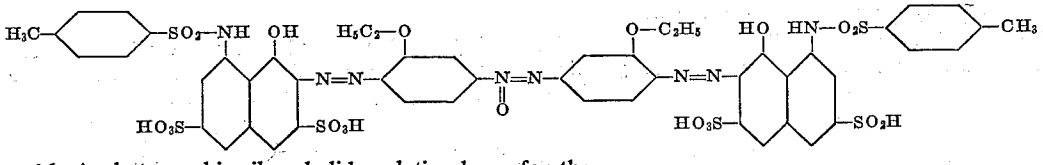
13. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



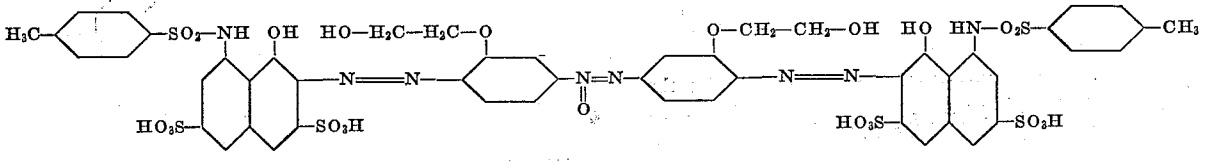
14. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



15. A photographic silver halide gelatine layer for the silver dyestuff bleaching methd containing as an image dyestuff the azoxy dyestuff of the formula



16. A photographic silver halide gelatine layer for the silver dyestuff bleaching method containing as an image dyestuff the azoxy dyestuff of the formula



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NORMAN G. TORCHIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,211,556 October 12, 1965

Walter Anderau

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 16, claim 3, for that portion of the formula reading

R_6-NN- read R_6HN-

column 17, claim 5, line 4 after the formula, for "1(3′-carboxyl-4′hy-" read -- 1-(3′-carboxy-4′hy- --; column 19, line 30, for "methd" read -- method --.

Signed and sealed this 26th day of July 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents