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PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC IMAGES BY THE SILVER DYESTUFF BLEACHING PROCESS AND PHOTOGRAPHIC LAYERS THEREFOR

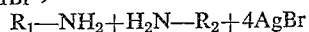
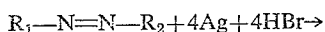
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 6 Claims. (Cl. 96—53)

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 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.

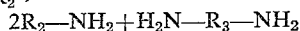
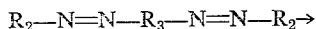
The method can be applied to a colored layer produced by coloring the layer-forming substance with the azo-dyestuff before the layer is formed or by coloring the finished layer on its support. The method can also be applied to multi-layer photographic materials.

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 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 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 amino-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 practically colorless decomposition products according to the following equation:



R_1 represents the radical of the diazo-compound obtained 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 component. In the case of disazo- or polyazo-dyestuffs there are also obtained as fission products diamines, for example:



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 image is converted into a dyestuff image, and this is very often undesirable.

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 multi-layer 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



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 $R-NH_2$, in which R has the meaning given above, with 5-pyrazolones.

As supplementary dyestuffs there are used in the process, for example, dyestuffs of the formula

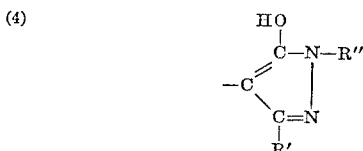


in which R_1 represents a benzene or naphthalene radical which is bound in the 1-position to the azo linkage and contains in the 2-position or advantageously in the 4-position as an electron-donating substituent a hydroxyl or amino group, and Py represents the radical of a 5-pyrazolone bound in the 4-position to the azo linkage. Among the dyestuffs 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



in which R₂ and Py each represent the radical of a 5-pyrazolone bound in the 4-position to the azo linkage, the radicals R₂ and Py being identical or different from each other.

The pyrazolone radicals Py and/or R₂ may, for example, correspond to the formula



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 last-mentioned 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.

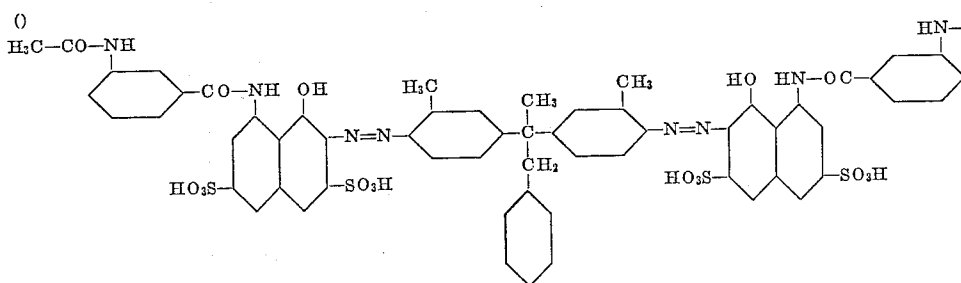
By this treatment the supplementary dyestuff is completely destroyed with the formation of colorless components or components capable of being removed by washing. Accordingly, there are obtained pure colors formed solely by image dyestuffs and pure whites at the colorless places, which is especially 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 gradation curves to be modified as desired.

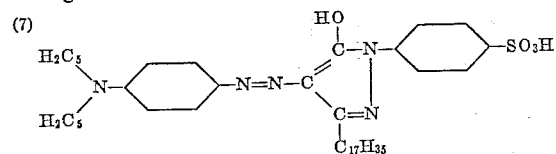
The following examples illustrate the invention, the parts and percentages being by weight:

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



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



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

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

5	Thiourea	grams	10
	Potassium bromide	do	12.5
	2:3-diaminophenazine	do	0.005
	Hydrochloric acid of 37% strength	cc	100
	Water to make 1 liter.		

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

		Grams	
15	Potassium ferricyanide	100	
	Boric acid	8	
	Sodium borate	4	
	Potassium bromide	50	
	Water to make 1 liter.		

20 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.

30 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.

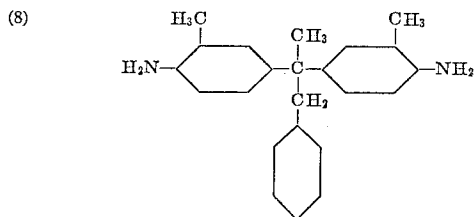
45 The 1-benzyl-1:1-di-(3'-methyl-4'-aminophenyl)-ethane used as starting material can be prepared as follows:

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-

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

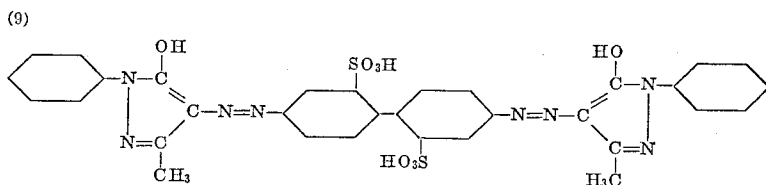


The acetyl-compound of this diamine melts at 237° C.

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.

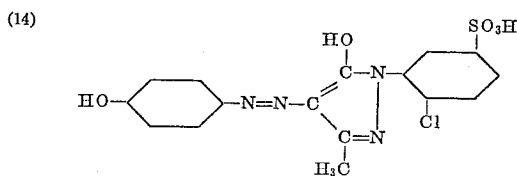
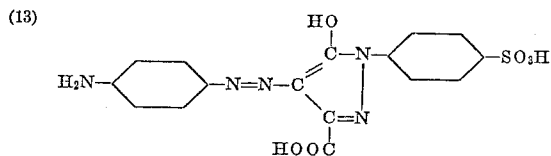
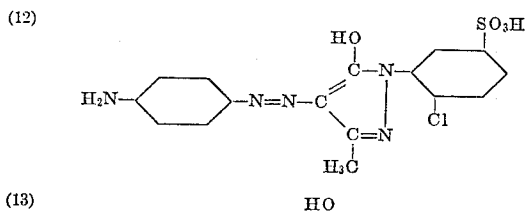
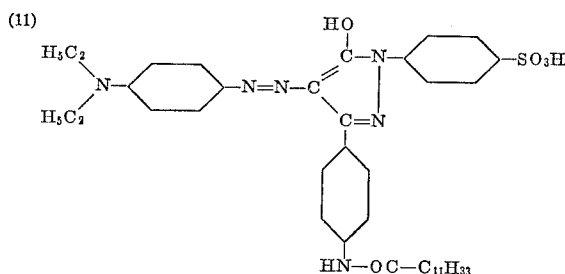
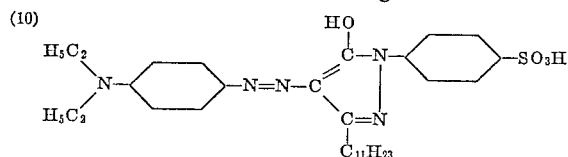
Example 2

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



and anhydrobiguanido-benzyl alcohol acetate.

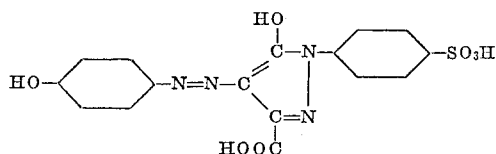
B. Upon other glass plates there were cast emulsions which contained the constituents mentioned under A and also 20 to 50% (calculated on the quantity of dyestuff of the Formula 9) of the dyestuff of the Formula 7 or one of the dyestuffs of the following formulae:



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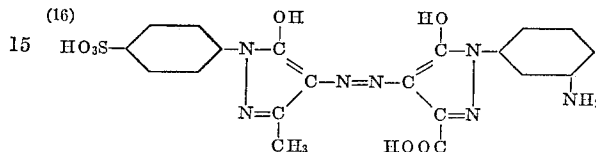
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30 (17)

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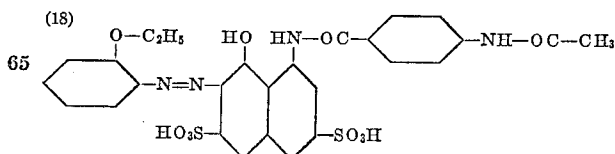
All the plates were developed, fixed, hardened and treated in a dyestuff bleaching bath as described in Example 1. The silver was then bleached out in 10 minutes in a bath which contained, per liter of water, 30 grams of potassium ferricyanide, 10 grams of potassium bromide and 10 grams of anhydrous 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

55 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.

60 (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.

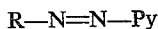
The photographic material so produced was processed 75 by one of the usual methods of carrying out the silver

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.

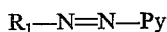
What is claimed is:

1. In a process for the production of color photographic 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 formula



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 positions 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 5-pyrazolone bound in 4-position to the azo linkage, and by destroying completely said supplementary dyestuff in an oxidizing bath following the bleaching bath.

2. 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 at least one supplementary dyestuff of the formula



in which R_1 represents a benzene radical which contains a hydroxyl group in para-position to the azo linkage and Py represents the radical of a 5-pyrazolone bound in 4-position to the azo linkage.

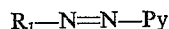
3. A bleachable photographic silver halide emulsion layer for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image formation, at the most an equal quantity of at least one supplementary dyestuff of the formula



in which R_1 represents a benzene radical which contains 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.

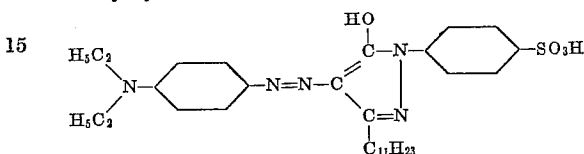
4. A bleachable photographic silver halide emulsion layer for the silver dyestuff bleaching method which contains in addition to at least one dyestuff serving for image

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

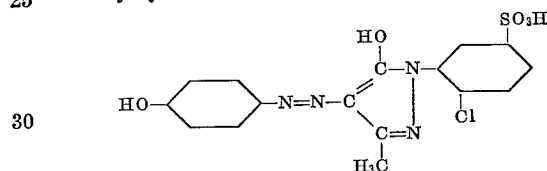


5. in which R_1 and Py each represents the radical of a 1-phenyl-5-pyrazolone bound in 4-position to the azo linkage, at least one of the phenyl radicals containing a sulfonic acid group.

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



6. 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



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PHILIP E. MANGIN, *Examiner*.