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PROCESS FOR PRODUCING COLOR PHOTOGRAPHS

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Int. Cl. G03c *7/16*
U.S. Cl. 96—53
8 Claims

ABSTRACT OF THE DISCLOSURE

The present invention provides an improvement in a process for producing color photographs by the silver dye bleach method. The improvement comprises treating photographic layers containing gelatine, a metallizable azo dyestuff fast to diffusion, being freed from metallic silver by oxidation, with a water soluble compound of a metal having an atomic number of at least 24 and at most 29. The photographs have an improved fastness to light which also is manifested by pure colors free from stain.

This is a continuation-in-part of our copending application Ser. No. 34,389, filed June 7, 1960, now abandoned.

The present invention provides an improvement in a process for producing color photographs by the silver dye bleach method. As is known, their poor fastness to light is a disadvantage of the known color photographs. This is particularly true of materials processed by the dye-forming development. It is, however, also true of the so-called silver bleaching out process in which the dyestuffs contained in the individual layers are bleached out depending on the quantity of silver produced photographically in the layer.

As will be explained hereinafter the unsatisfactory fastness to light of pictures produced by the silver dye bleaching method is attributable to various reasons. It can be substantially improved in the present process for making color photographs by the silver dye bleach method wherein a color image containing material, having at least one gelatine layer containing a metallizable azo dye and being resistant to diffusion, is freed from metallic silver by oxidation. The improvement comprises treating said material subsequent to said oxidation with a water soluble compound of a metal having an atomic number of at least 24 and at most 29 in an aqueous medium of pH 3.5 to 11.5.

Particularly advantageous results are in general obtained with compounds of cobalt, nickel and copper.

There may be used simple salts of the said heavy metals derived from an inorganic or organic acid, for example the chlorides, sulfates, nitrates, formates or acetates. Since, however, a strongly acidic reaction medium should not be used and the process is advantageously performed in an alkaline medium, it is of advantage to use a heavy-metal compound from which at such a pH value no precipitate results, that is to say preferably a water-soluble heavy metal compound containing the heavy metal bound in complex union.

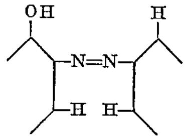
The heavy-metal atom may be present, for example, in the anion of a complex derived from an organic, colorless hydroxycarboxylic acid. As relevant examples may be mentioned the complexes consisting of an alkali metal salt or ammonium salt with a heavy metal salt of citric acid, lactic acid, tartaric acid or of a monocyclic ortho-hydroxycarboxylic acid of the benzene series such as 4- or 6-methyl-1-hydroxybenzene-2-carboxylic acid or preferably of salicylic acid not containing any further substituents.

Particularly suitable are also the heavy metal amine complex compounds derived from ammonia or a lower aliphatic amine such as methylamine, ethylamine, mono-, di- or triethanolamine, or from a pyridine base such as pyridine itself or from a picoline or from an amino-carboxylic acid such as a glycine.

Instead of dissolving a complex compound obtained in known manner for the treatment of the photographic material in water or in another suitable solvent, it may in some cases be prepared immediately before use or made up into a stock solution, for example by adding to an aqueous solution of copper sulfate tartaric acid and then sodium hydroxide solution until a weakly alkaline reaction is achieved, or by treating the copper sulfate solution with excess aqueous ammonia.

The present process may be performed with for example, a monoazo, disazo or polyazo dyestuff which may be free from, or preferably may contain, groups imparting solubility in water, more especially sulfonic acid groups. The tint depends on the individual purpose so that dyestuffs to be used prefentially are those of yellow, cyan, and magenta tint of extreme purity. Owing to the fact that the photographic material has to satisfy requirements quite different from those arising in the case of dyed textile materials, the stability of the metal-dyestuff complexes in an aqueous medium at an elevated temperature is of minor importance so that there is no objection to using in the present case dyestuffs containing groups capable of forming metal complexes that are far too unstable for use in dyeing textile materials and accordingly produce complexes that are not fast to washing.

Thus, for example, there are quite generally suitable dyestuffs that contain at least one hydroxyl group (including an enolizable ketomethylene group) in a vicinal position to an azo linkage. For the reasons given above the other vicinal position need not contain a substituent that participates in or promotes the complex formation. Thus, for example, the complex-forming azo dyestuff may contain an atomic grouping of the formula



Apart from the azo dyestuffs mentioned above there may be used with advantage also those which contain at least one azo linkage carrying a substituent in vicinal position to the other nitrogen atom, said substituent being capable of forming together with the hydroxyl group a complex heavy-metal compound. As examples of complex-forming groups of this composition may be mentioned ortho-hydroxy-ortho'-alkoxy groups, more especially the ortho-hydroxy-ortho'-methoxyazo group, the ortho-hydroxy-ortho'-aminoazo group, the ortho-hydroxy-ortho'-carboxymethoxy-azo group, the ortho-hydroxy-ortho'-carboxyazo grouping and the ortho:ortho'-dihydroxyazo grouping.

There may also be used dyestuffs in the case of which the complex may be formed, instead of at the substituents in vicinal positions to an azo linkage, for example, at an 8-hydroxyquinoline radical or more especially at a salicylic acid grouping. It will be readily understood that the dyestuffs may contain two or more identical or different groups capable of forming complexes.

A large number of dyestuffs suitable for the present process is known and they can be made by conventional, as such known methods.

According to the present process the treatment with the heavy-metal compound is performed at a pH value of at least 3.5, advantageously of at least 4 and of at most 11.5. At these pH values heavy-metal-dyestuff complexes are still stable, while in a more strongly acidic medium they decompose extensively or even completely, or are at best only formed in a minor amount. For this reason it is of advantage to perform the treatment with the heavy-metal compound after an optional treatment in a strongly acidic medium.

In the case of some dyestuffs the after-treatment is accompanied by slight shift in tint. This shift must be taken into consideration in selecting the dyestuff to be used.

The present invention offers considerable advantages over the known processes. While very many dyestuffs that are fast to light are known, only some of them are suitable for use in the silver dye bleach process because they must satisfy numerous requirements arising from other aspects of the photographic process. Thus, for example, the dyestuffs to be used in the silver dye bleach process must be compatible with the individual constituents of the silver halide emulsion; they must satisfy certain spectral conditions, and they must lend themselves to bleaching out. Many dyestuffs that are fast to light are unsuitable because they have a strong desensitizing effect on the silver halide emulsion. The necessity of increasing the fastness to light is further emphasized by the fact that the fastness to light depends very much on the substratum so that, for example, certain dyestuffs that are fast to light when applied to cotton are much less fast to light in gelatine. More especially, the different additives required to be present in a gelatine emulsion or in a layer adjacent thereto such, for example as organic bases, which act as sensitizers or have the purpose of counteracting the tendency of the dyestuffs to diffuse, have a disadvantageous effect on the fastness to light of the dyestuffs in the finished image. Many of these additives are needed to be present only during the manufacture of the light-sensitive photographic material or during the development process, but they cannot always be washed out of the material; others, such, for example, as the scission products of dyestuffs and filter dyestuffs, arise only during developing. The reduction of the light fastness to dyestuffs due to the presence of organic bases that cannot be washed out such, for example, as quaternary nitrogen bases or guanidine bases, can be annulled by an after-treatment with a heavy-metal compound. It is a moot point whether the increase in fastness to light is attributable to the mere presence of the heavy-metal compound in the layer or to the formation of dyestuff-metal complexes or to a reaction with any base present, or to a combination of several of these factors.

When a base is present for the purpose of increasing the resistance of the dye to diffusion during casting and developing, the change in this base by forming a compound with the heavy-metal towards the end of the process is no longer disadvantageous since there is no need for the dyestuff to resist washing out in the finished image. There may also be added to the after-treatment bath besides the heavy-metal compound an organic base, for example a biguanide, whereby the resistance to diffusion is maintained without impairing the advantageous effect of the heavy-metal compound on the fastness to light.

After-treatment according to the present process not only enhances the fastness to light of the dyestuff as such, but it may also effect a chemical change in the substratum and in the additives so that they lose their harmful influence. The advantages in this connection are more especially that the fastness to light does not materialize until after the after-treatment, while during the manufacture of the photosensitive material and during its development the light fastness of the dyestuff need not be considered; as a matter of fact it is even possible to use measures that jeopardize the fastness to light, but that can be annulled or eliminated by the after-treatment. Inter alia, it is possible to incorporate in the layers dyestuffs that are at first free from heavy metal and thus have less fastness to light but which have better compatibility with the emulsion; by virtue of their constitution do not diffuse or can be made resistant to diffusion; lend themselves well to bleaching and are thus capable of satisfying the requirements involved in the treatment process. The after-treatment with a heavy-metal compound converts the dyestuffs at the end of the treatment into a form of considerably better fastness to light.

If certain metallizable dyestuffs fast to light were incorporated in the emulsion from the start, other properties of the material, such, for example, as is speed, would be substantially impaired. Moreover, the fastness to light of these metallized dyestuffs would be destroyed by certain steps involved in the treatment such, for example, as the use of strongly acidic treatment baths.

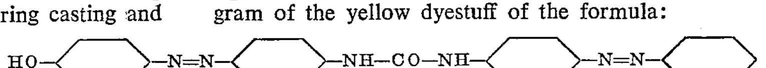
As will be realized from the foregoing it is possible to produce by way of the present invention by the silver dye bleach process color photographs that contain at least one heavy-metal compound of an azo dyestuff from which complex the metal is easy to eliminate in a strongly acidic medium.

In the silver dyestuff bleaching operation, the azo dyestuffs are reduced to ortho-hydroxyaminoaryl or ortho-diaminoaryl compounds, and it is generally known that such ortho-disubstituted compounds are easily oxidizable. The largest possible quantity of the reduction product is obtained where the dyestuffs are completely bleached out and where the white parts of the image should be. As is also known, the ortho-hydroxyamino- and diamino compounds easily form colored oxidation compounds. It was to be expected that the treatment with metallizing agents would stain the color images and particularly in the parts which should be white. It is just here that the largest quantity of undesirable reduction products is to be found, and just here, too, that the colored oxidation products are the least tolerable. However, quite surprisingly, no such staining takes place in the present process.

It is known to treat textile dyeings with certain agents yielding metal. It is also known to treat certain photographic materials, used in transfer processes, with metallizing agents. However, in the materials to be treated in accordance with these known methods no oxidizable ortho-hydroxyamino- and diamino compounds are present.

Example 1

A film is coated with a gelatine layer containing per square meter 2.5 grams of silver as silver bromide, 0.6 gram of the yellow dyestuff of the formula:



$$HO-C_6H_3(COONa)-N{=}N-C_6H_4-NH-CO-NH-C_6H_3(OCH_3)-N{=}N-C_6H_4-SO_3Na$$

and 1.0 gram of anhydro-biguanido benzyl alcohol acetate.

The film is exposed in contact with a stepped spectroscope wedge, developed in a metol-hydroquinone developer and fixed. The film is then treated in a dye bleaching bath containing per liter—

Hydrochloric acid of 36% strength	cc	100
Potassium bromide	grams	100
Thiourea	do	50
2:3-diaminophenazine	milligrams	2

whereby the dyestuff is destroyed in the areas where metillic silver is present. The excess silver is oxidized in a bath containing per liter—

Copper sulfate	grams	100
Sodium chloride	do	100
Hydrochloric acid of 36% strength	cc	100

and eliminated in a fixing bath. Between all baths and at the end the film is thoroughly rinsed.

A yellow color image obtained in this manner is after-treated for 3 minutes in a solution consisting of—

Nickel sulfate	grams	1.0
Monoethanolamine	do	2.0
Water	cc	100

rinsed for a short time and dried. Another image obtained by the identical method is not after-treated and merely dried after rinsing.

Two images obtained in this manner were exposed for 56 hours in a fadeometer, whereby one area of the film that was not after-treated and had an initial density of 1.0 (measured in blue light) was completely bleached out while the identical area of the image on the film after-treated in the nickel bath only lost 15% of its density and did not suffer a change in tint.

Example 2

A film is cast which contains, instead of the dyestuff used in Example 1, the yellow dyestuff prepared by coupling on both sides tetrazotized benzidine-2:2′-disulfonic acid with 1-phenyl-3-methyl-5-pyrazolone. The film is developed in identical manner and after-treated in an ammonical bath containing 10% of cobalt nitrate. When the film so after-treated is compared in a fadeometer or in sunlight with a film that has not been so after-treated but is otherwise identical, it is noticed that the after-treated film is very much faster to light than the film that has not been after-treated.

Example 3

The dyestuff of Example 1 is replaced by the magenta dyestuff obtained by coupling diazotized 1-amino-2-ethoxybenzene with 1-(para-acetylaminobenzoylamino)-8-hydroxy-naphthalene-3:6-disulfonic acid. In other respects the procedure of Example 1 is followed. After-treatment with the nickel bath of Example 1 or with the cobalt bath of Example 2 improves the fastness to light considerably. Instead of the afore-mentioned after-treatment baths one of the following baths can be used with equal success:

(A)

Copper sulfate	grams	1
Salicylic acid	do	0.5
Water	cc	100

Sodium carbonate to raise the pH value to 4.3.

(B)

Copper sulfate	grams	2
Monoethanolamine	do	2
Water	cc	100

(C)

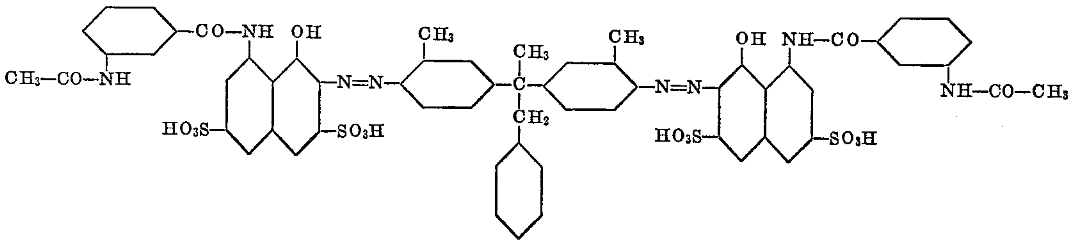
Copper sulfate	grams	1
Ammonia (28% strength)	cc	2
Water	cc	100

(D)

Copper sulfate	grams	2
Salicylic acid	do	1
Water	do	100
Sodium carbonate to raise the pH value to 4.3.		
Anhydro-biguanido benzyl alcohol acetate	grams	1

Example 4

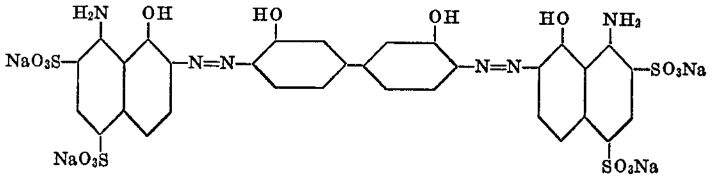
The dyestuff of the formula:



is dissolved in water, the solution is added to a silver bromide emulsion in gelatine and cast as a layer. Exposure and development are as described in Example 1. After-treatment in one of the aforementioned baths, for example in bath (B) of Example 3, improves the fastness to light substantially.

Example 5

The dyestuff of the formula:

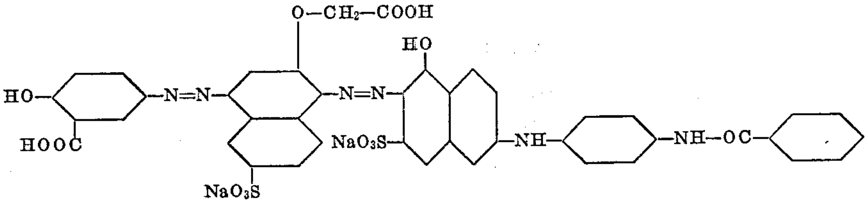


(obtained by coupling tetrazotized 3:3′-dihydroxy-4:4′-diaminodiphenyl with 1-amino-8-hydroxynaphthalene-2:4-disulfonic acid in the presence of calcium hydroxide and pyridine) is dissolved in gelatine and rendered fast to diffusion, for example with anhydro-biguanido benzyl alcohol acetate. When this dyestuff is used in the usual manner in the silver dye bleach process it produces a blue component image which becomes fast to light on after-treatment in a bath containing copper acetate, for example for 30 minutes at 18° C. in a bath containing 30 grams of crystalline copper acetate dissolved per liter of water.

Instead of the copper acetate solution there may be used a solution of sodium copper acetate or glycine copper having an equal content of copper. A similar improvement in the fastness to light is also achieved by using instead of the copper acetate solution a solution that contains 20 to 40 grams of potassium titanium sulfate per liter of water.

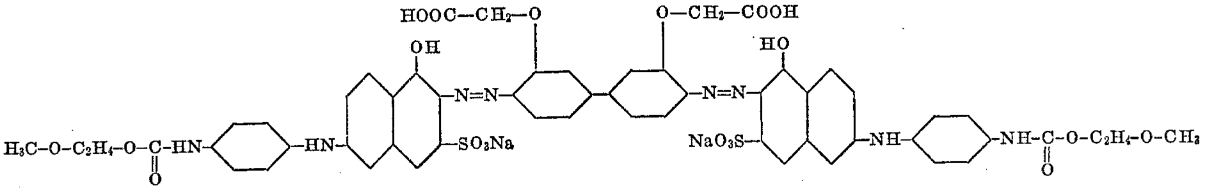
Example 6

The dyestuff specified in Example 5 may be replaced by the dyestuff of the formula:

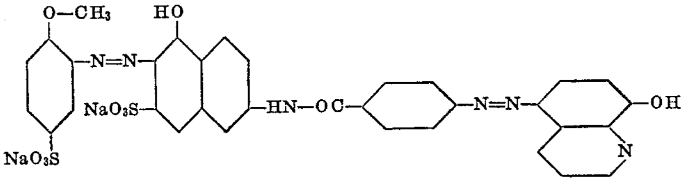


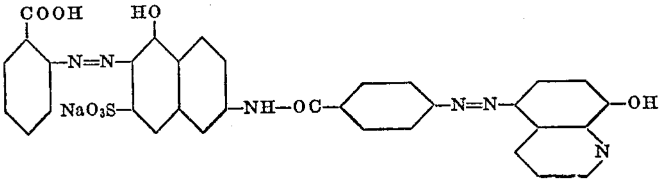
By using a copper salt according to Example 5 or cadmium acetate, cobalt acetate or nickel acetate, a greenish blue image is obtained which is fast to light.

A blue image fast to light is also obtained by after-treating with a copper salt, a nickel salt or basic chromium sulfate, with the dyestuff of the formula:



Red images fast to light are obtained with the dyestuffs of the formulae:





by after-treatment with a salt of manganese, cobalt or nickel.

Example 7

On a film four gelatine layers are cast in the following order of succession:

(1) A red-sensitive silver bromide emulsion containing a dyestuff according to Colour Index Direct Green 27, as well as anhydro-biguanido benzyl alcohol acetate.

(2) A green-sensitive layer containing the additives specified in Example 3.

(3) A yellow filter layer.

(4) A non-sensitized layer containing the additives mentioned in Example 1.

The film is treated as described in Example 1. After-treatment with the nickel bath described in Example 1 considerably improves the fastness to light of all dyestuffs.

What is claimed is:

1. In a process for making color photographs by silver dye bleach method wherein a color image-containing material, having at least one gelatine layer containing metallizable azo dye and being resistant to diffusion, is freed from metallic silver by oxidation, the improvement comprising treating said material subsequent to said oxidation with water-soluble compound of metal having an atomic number of at least 24 and at most 29 in aqueous medium of pH 3.5 to 11.5.

2. In a process for making color photographs by silver dye bleach method wherein a color image-containing material, having at least one gelatine layer containing metallizable azo dye with at least one salicylic acid group and being resistant to diffusion, is freed from metallic silver by oxidation, the improvement comprising treating said material subsequent to said oxidation with water-soluble compound of metal having an atomic number of at least 27 and at most 29 in aqueous medium of pH 3.5 to 11.5.

3. In a process for making color photographs by silver dye bleach method wherein a color image-containing material having at least one gelatine layer containing metallizable azo dye with at least one hydroxyl group in vicinal position to said azo group and being resistant to diffusion, is freed from metallic silver by oxidation, the improvement comprising treating said material subsequent to said oxidation with water-soluble compound of metal having an atomic number of at least 27 and at most 29 in aqueous medium of pH 3.5 to 11.5.

4. In a process for making color photographs by silver dye bleach method wherein a color-image containing material having at least one gelatine layer containing metallizable azo dye, said dye having hydroxyl group in vicinal position to one nitrogen atom of said azo group and a group capable of forming complex metal compound together with said hydroxyl group in vicinal position to the other nitrogen atom and being resistant to diffusion, is freed from metallic silver by oxidation, the improvement comprising treating said material subsequent to said oxidation with water-soluble compound of metal having an atomic number of at least 27 and at most 29 in aqueous medium of pH 3.5 to 11.5.

5. Process of claim **1** wherein said metal is present in said aqueous medium as a complex ion.

6. Process of claim **1** wherein said compound is monocyclic ortho-hydrocarboxylic acid of the benzene series.

7. Process of claim **1** wherein said compound is an amine.

8. Process of claim **1** wherein said metal has an atomic number of 27 to 29.

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J. TRAVIS BROWN, *Primary Examiner.*

U.S. Cl. X.R.

96—20