United States Patent Office 3,156,561 Patented Nov. 10, 1964

3,156,561

METHOD OF PRODUCING COLOR PHOTOGRAPHIC PICTURES

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No Drawing. Filed June 1, 1959, Ser. No. 817,068
Claims priority, application Switzerland, June 3, 1958, 60,178; Apr. 16, 1959, 72,135
16 Claims. (Cl. 96—20)

This invention relates to a method of producing color photographic pictures by the silver-dyestuff bleaching process.

For making muti-color photographic pictures consisting of component color images the so-called silver-dyestuff bleaching process has been known for a long time. In this process the individual component color images are first produced as silver images in layers that are either previously homogeneously colored with dyestuff or are homogeneously colored after production of the silver image. The dyestuff is then bleached in a dyestuff bleaching operation locally in accordance with characteristics of the image depending on the distribution of silver in the component image, the dyestuff being destroyed at those parts of the image where silver is present. In the production of multi-color pictures, especially the usual three-color or four-color pictures, the bleaching operation is carried out in a plurality of different colored layers or media. For the purpose of color balance it is desirable that it should be possible to adjust the gradation of the individual color component images relatively to one another. The necessity for such a balance arises from the multiplicity of variables, such as the dyestuffs used, the original silver emulsions and intermediate stages of the process. Fundamentally, it is possible to influence this color balance by appropriately selecting the gradation of the silver image before the dyestuff bleaching operation. It is also known to add substances that accelerate or retard the speed at which the dyestuff is bleached. Notwithstanding these proposals there is considerable difficulty in securing satisfactory balance of the multi-color material, and the attainment of such a balance is endangered or rendered impossible by unavoidable variations in the manufacture and treatment of the material.

The present invention provides a method for producing by the silver-dye bleaching process photographic pictures composed of at least two component color images, wherein at least two dyestuff bleaching baths are used in succession for bleaching the several component color images and at least one of the dyestuff bleaching baths has a substantially selective action.

Advantageously, the second dyestuff bleaching bath bleaches out substantially only the dyestuff of the residual component image not bleached by the first bath.

By the use of such successive dyestuff bleaching baths, which have a bleaching action only upon a part of the component images of the material, there is considerably wider scope for varying the bleaching operations as they are separated from each other. It thus becomes possible to perform the bleaching-out operations in the individual layers independently of one another so that a desired result can be attained, for example, the balancing of the color gradation of a three-color picture on a neutral grey scale. The balance may first be determined empirically by tests for a certain material, and then subsequently used for the practical work without change, that is to say, in the predetermined form. Alternatively, the balance may be adjusted individually after the image has been treated, for example, by so controlling the second dyestuff bleaching bath in accordance with the component image obtained by the first dyestuff bleaching bath that the desired balance is obtained.

In carrying out the method of this invention it is of advantage to incorporate in the successive baths substances which exert a different action on the bleaching-out of one or some of the dyestuffs present in the several layers. This can be brought about, for example, by the use in succession of an acid and an alkaline bleaching bath, for example, an alkaline stannite solution. Preferably, however, this varying action, especially an accelerating or retarding action, is achieved by incorporating in at least one bath serving for bleaching-out one or more dyestuffs a substance which has an accelerating action on the bleaching of the dyestuffs associated with one or other of the component color images and/or simultaneously a retarding and/or inhibiting action on the bleaching of at least one dyestuff in another component color image. These substances, some of which can be regarded as selective bleaching catalysts, are, for example, riboflavine, lumazine and alloxazine. These substances and processes for making them are described, inter alia, in British specifications Nos. 651,124 and 657,374. Further substances suitable as selective catalysts are given in the examples that follow. Furthermore, for example, the content of thiourea in the bleaching bath influences the bleaching of different dyestuffs to different degrees. Accordingly, thiourea can also be used in the method of this invention as a selective accelerating or retarding substance. Also mild oxidizing agents, tartrazine, nitrobenzene sulfonic acid etc., such as are described, for example, in British specifications Nos. 539,190, 539,391 and 539,509, as additions to bleaching baths, act in the same manner.

A further advantage of the method of this invention in which the bleaching is divided between two successive baths, is that one or more other baths of any kind may be interposed between the two color bleaching baths, which additional baths may serve to act upon one or some of the component images. This is possible owing to the fact that after the first dyestuff bleaching bath some of the component images, especially the component image bleached in the first bath, are present as dyestuff images or as dyestuff images and silver images, and the others, namely the unbleached component images, are present only as silver images. Thus, it becomes possible to interpose one or more steps which act only on the silver images, especially silver images that have not yet been used for bleaching dyestuffs. Thus, for example, there may be interposed between the first and second dyestuff bleaching baths a silver reducing bath, whereby the gradation of the dyestuff image formed in the succeeding second dyestuff bleaching bath can be selectively influenced. Depending on the nature of the reducer used and its action on the various parts (foot, linear part or shoulder) of the characteristic curve of the silver image that remains, it is possible to influence in various ways the gradation of the dyestuff image obtainable in the next succeeding bleaching bath, and so achieve to a very great extent the correspondence of color gradation of the color images necessary for good color reproduction.

An important feature of the invention therefore lies in the use of a plurality of successive dyestuff bleaching baths, each of which baths produces only a part of a color image.

The advantages of the method of this invention as compared with the known methods are obvious. The dyestuffs generally used are not bleached in an identical manner in the bleaching bath. Thus, for example, if an image constituted by a dyestuff that is difficult to bleach is to be adequately bleached a more easily bleachable dyestuff is bleached out too strongly so that it yields an image of too steep gradation. By using a single bleaching bath it is only possible to control the degree of bleaching of all the layers at the same time. Thus, a method involving a

single bleaching bath fails when a photographic material having more than one layer is used, for example, the usual 3-color layer materials used at the present time, because it is not possible selectively to control the bleaching process in the individual layers, for example, by simple variation in the period of action of the bleaching bath. The possibility afforded by the method of this invention of controlling the bleaching process in the several layers is thus of fundamental importance for achieving color balance and therefore an image of good quality.

The present invention includes not only the whole method, but also the steps of the method. Thus, for example, the multi-color material may be bleached in any of the successive bleaching baths for a period long enough to bleach completely at least one of the dyestuffs so that silver and dyestuff do not exist simultaneously at any part of the image. However, the treatment in the individual bleaching baths may be interrupted at an earlier stage when none or only a few of the dyestuffs capable of being bleached by a given bleaching bath have been completely bleached, or the bleaching may be interrupted prematurely for some of the dyestuffs and completed for the other dyestuffs, the baths being used in any desired order of succession.

The invention also includes the use in the dyestuff bleaching baths of substances which partially retard or partially accelerate the bleaching-out of different dyestuffs. If desired, such selective bleaching of the several color layers may also be brought about by adjusting certain conditions in the baths, for example, temperature, pH-value, etc. The successive bleaching baths may be alkaline or acid, or one of the baths may be alkaline and another may be acid. The photographic material may be original or copy material, pictures to be viewed by refracted or transmitted light, cinematograph film or material for instantaneous photography. The photographic material may be composed of separate layers or mixed granular emulsions.

The following examples illustrate the invention:

EXAMPLE 1

A three-layer film was used having a red-sensitized layer, which was dyed with a dyestuff described in Schultz, Farbstofftabellen, 7th Edition, Vol. II, pages 220–222—E.I. 142 (C.I. Direct Green 27), then a green-sensitized layer, which was dyed with a dyestuff described in Schultz, Farbstofftabellen, 7th Edition, Vol. II, page 48—E.I. 79, (C.I. Acid Red 131) and finally a non-sensitized layer, which was dyed with a yellow dyestuff obtained by tetrazotizing benzidine-2:2'-disulfonic acid and coupling the tetrazo compound with 1-phenyl-3-methyl-pyrazolone-(5). Each of the three dyestuffs was precipitated in the emulsion fast to diffusion by means of an organic base. The base was obtained as described in Example 2 of the United States Patent No. 2,317,184. The photographic material was exposed behind a stepped wedge in adjacent areas with blue, green and red light, and then developed and fixed. There were obtained three silver images one each in the yellow, purple-red and blue-green layers, respectively. The bleached baths mentioned below were used for bleaching, and then the excess of silver was oxidized in a ferricyanide bath and eliminated in a fixing bath. Hardening was carried out in a formaldehyde bath before bleaching, and the material was thoroughly washed with water after treatment in each of the baths.

Bleaching Baths

A

100 grams of potassium bromide and
100 cc. of pure concentrated hydrochloric acid, made up to
1 liter with water

B

100 grams of potassium bromide and
100 cc. of pure concentrated hydrochloric acid, 0.05 gram of riboflavine made up to
1 liter with water

C

100 grams of potassium bromide
100 cc. of pure concentrated hydrochloric acid, alloxazine saturated (less than 0.05 gram) made up to
1 liter with water

D

50 grams of thiourea
100 cc. of pure concentrated hydrochloric acid made up to
1 liter with water

E

100 grams of potassium bromide and
100 cc. of concentrated hydrochloric acid,
20 grams of hydroquinone made up to
1 liter with water

F

100 grams of potassium bromide and
100 cc. of concentrated hydrochloric acid
20 grams of amidol made up to
1 liter with water

The results of bleaching are given in the following table. The symbols in the table have the following meanings:

−=no bleaching
+=a trace of a bleaching
++=feeble bleaching
+++=medium bleaching
++++=a strong bleaching

of the particular layer.

Bath	A	B	C	D	E	F
Duration, min.	90	60	10	20	30	30
Yellow	+++	++	−	++++	++++	+
Purple	+++	+++	+	++++	++++	+
Blue-green	+	++++	++++	+	+	++++

Thus, riboflavine and amidol has an accelerating action towards the blue-green image and a very slight retarding action towards the yellow image as compared with the bath A that was free from additions. The same applies in higher degree to alloxazine, which also retards the bleaching of the purple image. On the other hand, thiourea and hydroquinone have an accelerating action towards the yellow and purple images.

EXAMPLE 2

The starting material used in Example 1 was treated in the baths A, B and C described in that example for 60 minutes at 20° C. in each bath. In baths A and B approximately the same same degree of bleaching was achieved in the case of the purple image, and in bath C the bleaching was considerably less. Accordingly, the alloxazine present in bath C acted as a negative catalyst towards the purple layer and as a positive catalyst towards the blue-green layer.

EXAMPLE 3

The starting material used in Example 1 was treated first for 15 minutes in bath D, and then for 3 minutes in bath C, whereby a satisfactory harmony between the color gradations in the three layers was obtained.

EXAMPLE 4

The starting material used in Example 1 was bleached in bath E for 20 minutes, then treated in Farmer's reducer for 5 minutes, and was finally bleached for 15 minutes in bath F. A very good balance of the three-color gradations was obtained.

EXAMPLE 5

The starting material described in Example 1 was exposed, developed and fixed in the manner described in that example. The material so treated was then treated first for 5 minutes in the bleaching bath H described below and then for 50 minutes in the bleaching bath I described below.

H

100 grams of potassium bromide and
100 cc. of concentrated hydrochloric acid
2 milligrams of 2:3-amino-oxyphenazine made up to 1 liter with water

I

100 grams of potassium bromide,
50 grams of thiourea
100 cc. of concentrated hydrochloric acid made up to 1 liter with water

Silver still present in the material was then removed in the manner described in Example 1. In the color material so obtained all three of the component color images had gradations balanced relatively to one another in the necessary manner.

The same satisfactory result was obtained by treating the developed material first for 30 minutes in bath I and then for 10 minutes in bath H.

In a control experiment the same photographich material developed in the same manner was treated solely in a bleaching bath having the following composition:

G

100 grams of potassium bromide
50 grams thiourea
100 cc. of concentrated hydrochloric acid
2 milligrams of 2:3-amino-oxyphenazine made up to 1 liter with water

It was found that even by varying the bleaching periods it was not possible to obtain a balance between the color gradations. The gradation of the cyan image was always steeper than that of the purple and yellow images. Similarly it was not possible to obtain a satisfactory result by bleaching solely in bath H or solely in bath I. When the bleaching was carried out solely in bath H, the gradations of the purple and yellow images were too flat and the gradation of the cyan image was too steep. When bleaching was carried out solely in bath I the gradation of the cyan image was too flat compared with the gradation of the purple and yellow images.

EXAMPLE 6

The starting material used in Example 1 was bleached first for 30 minutes in bath I. In this bath the yellow and purple images were formed and at the same time a relatively large part of the silver image was removed, so that after a little practice the color balance of the image could be visually assessed (or if desired determined by densitometric measurement). Thus, the subsequent bleaching in bath H could be carried out, after repeated inspection, until the cyan image had been bleached to the desired extent. The image was then finished by removing the silver still present.

What is claimed is:

1. In a process for producing colored photographic pictures composed of at least two component color images by the silver-dyestuff bleaching process, wherein (*a*) by exposure and development silver images representing the component color images are produced in a photographic material, each image being in close spatial relationship with an appertaining dyestuff, and wherein (*b*) said dyestuffs are bleached in dependence on the appertaining silver images to produce dyestuff images, the improvement consisting essentially of subjecting the dyestuffs contained in the photographic material, after full formation of the silver images, to bleaching out treatment comprising at least two successive operations in dyestuff bleaching baths, each of which baths exerts a different bleachng action on at least one and the same component image, thereby acceleratedly bleaching out dyestuff of at least one, but less than all, of the component images in at least one of said bleaching operations, and bleaching out dyestuff of from at least the remaining up to all of said component images in at least one other bleaching operation; and so adjusting the accelerated bleaching to the other bleaching as to yield the predetermined balance between the gradations of the different color component images.

2. In a process for producing colored photographic pictures composed of at least two component color images by the silver-dyestuff bleaching process, wherein (*a*) by exposure and development silver images representing the component color images are produced in different and differently dye layers of a photographic material, and wherein (*b*) dyestuffs of the different layers are bleached in an image-like manner in dependence on the silver images contained in said layers to produce from silver-dyestuff images pure dyestuff images therein, the improvement consisting essentially of subjecting the dyestuffs contained in different component images of the photographic material, after full formation of the silver images, to bleaching out treatment comprising at least two successive operations in dyestuff bleaching baths, each of which baths exerts a different bleaching action on at least one and the same component image, thereby acceleratedly bleaching out dyestuff of at least one, but less than all, of the component images in at least one of said bleaching operations, and bleaching out dyestuff of from at least the remaining up to all of the component images in at least one other bleaching operation; and so adjusting the accelerated bleaching to the other bleaching as to yield the predetermined balance between the gradations of the color component images in different layers.

3. A method as claimed in claim 2, wherein the first dyestuff bleaching operation bleaches out in accordance with the image characteristics substantially only dyestuff of at least one, but less than all of the component images and the second dyestuff bleaching operation bleaches out substantially only dyestuff of the remaining component images.

4. A method as claimed in claim 2, wherein the first dyestuff bleaching operation bleaches out in accordance with the image characteristics the dyestuffs of all the component images and the second dyestuff bleaching operation bleaches out substantially only the dyestuff of at least one, but less than all of the component images.

5. A method as claimed in claim 2, wherein the second dyestuff bleaching operation bleaches out in accordance with the image characteristics the dyestuffs of all the component images and the first dyestuff bleaching operation bleaches out substantially only the dyestuff of at least one, but less than all of the component images.

6. A method according to claim 2 wherein the bleaching bath used for bleaching out the dyestuff of at least one, but less than all of the component images contains a substance that accelerates the bleaching out of the dyestuff of one component image and simultaneously retards the bleaching of the dyestuff of at least one other component image, which substance is a member selected from the group consisting of riboflavine, lumazine, alloxazine, amidol, hydroquinone, thiourea and 2:3-amino-oxyphenazine.

7. A method as claimed in claim 6, wherein the said substance is riboflavine.

8. A method as claimed in claim 6, wherein the said substance is lumazine.

9. A method as claimed in claim 6, wherein the said substance is alloxazine.

10. A method as claimed in claim 6, wherein the said substance is amidol.

11. A method as claimed in claim 6, wherein the said substance is hydroquinone.

12. A method according to claim 2, wherein there is interposed between two successive bleaching operations at least one silver-reducing operation that affects only a silver image as yet unbleached.

13. A method according to claim 2, wherein the bleaching bath used for bleaching out the dyestuff of at least one, but less than all of the component images contains a substance that accelerates the bleaching out of the dyestuff of one component image and simultaneously inhibits the bleaching of the dyestuff of at least one other component image, which substance is a member selected from the group consisting of riboflavine, lumazine, alloxazine, amidol, hydroquinone, thiourea and 2:3-amino-oxyphenazine.

14. In a process for producing colored photographic pictures composed of a three component color image by the silver-dyestuff bleaching process, wherein (I) by exposure and development silver images representing the component color images are produced in different and differently dyed layers of a photographic material, and wherein (II) dyestuffs of the different layers are bleached in an image-like manner in dependence on the silver images contained in said layers to produce from silver-dyestuff images pure dyestuff images therein, the improvement wherein the three component color image is produced by means of

(A) a red-sensitized layer containing as dyestuff Colour Index Direct Green 27,

(B) a green-sensitized layer containing as dyestuff Colour Index Acid Red 131,

(C) a non-sensitized layer containing the yellow disazo dyestuff obtained by coupling tetrazotized benzidine-2:2'-disulfonic acid with 1-phenyl-3-methyl-pyrazolone-(5),

which improvement consists essentially of subjecting the dyestuffs contained in different component images of the photographic material, after full formation of the silver images, to bleaching out treatment comprising two successive bleaching operations in different dyestuff bleaching baths, one bleaching bath containing alloxazine and the other bleaching bath containing thiourea, each of said baths exerting a different bleaching action on at least one and the same component image, thereby acceleratedly bleaching out dyestuff of at least one, but less than all, of the component images in at least one of said bleaching operations, and bleaching out dyestuff of from at least the remaining up to all of the component images in the other bleaching operation; and so adjusting the accelerated bleaching to the other bleaching as to yield a predetermined balance between the gradations of the color component images in the different layers.

15. In a process for producing colored photographic pictures composed of a three component color image by the silver-dyestuff bleaching process, wherein (I) by exposure and development silver images representing the component color images are produced in different and differently dyed layers of a photographic material, and wherein (II) dyestuffs of the different layers are bleached in an image-like manner in dependence on the silver images contained in said layers to produce from silver-dyestuff images pure dyestuff images therein, the improvement wherein the three component color image is produced by means of

(A) a red-sensitized layer containing as dyestuff Colour Index Direct Green 27,

(B) a green-sensitized layer containing as dyestuff Colour Index Acid Red 131,

(C) a non-sensitized layer containing the yellow disazo dyestuff obtained by coupling tetrazotized benzidine-2:2'-disulfonic acid with 1-phenyl-3-methyl-pyrazolone-(5),

which improvement consists essentially of subjecting the dyestuff contained in different component images of the photographic material, after full formation of the silver images, to bleaching out treatment comprising two successive bleaching operations in different dyestuff bleaching baths, one bleaching bath containing amidol and the other bleaching bath containing hydroquinone, each of said baths exerting a different bleaching action on at least one and the same component image, thereby acceleratedly bleaching out dyestuff of at least one, but less than all, of the component images in at least one of said bleaching operations, and bleaching out dyestuff of from at least the remaining up to all of the component images in the other bleaching operation; and so adjusting the accelerated bleaching to the other bleaching as to yield a predetermined balance between the gradations of the color component images in the different layers.

16. In a process for producing colored photographic pictures composed of a three component color image by the silver-dyestuff bleaching process, wherein (I) by exposure and development silver images representing the component color images are produced in different and differently dyed layers of a photographic material, and wherein (II) dyestuffs of the different layers are bleached in an image-like manner in dependence on the silver images contained in said layers to produce from silver-dyestuff images pure dyestuff images therein, the improvement wherein the three component color image is produced by means of

(A) a red-sensitized layer containing as dyestuff Colour Index Direct Green 27,

(B) a green-sensitized layer containing as dyestuff Colour Index Acid Red 131,

(C) a non-sensitized layer containing the yellow disazo dyestuff obtained by coupling tetrazotized benzidine-2:2'-disulfonic acid with 1-phenyl-3-methyl-pyrazolone-(5),

which improvement consists essentially of subjecting the dyestuffs contained in different component images of the photographic material, after full formation of the silver images, to bleaching out treatment comprising two successive bleaching operations in different dyestuff bleaching baths, one bleaching bath containing 2:3-amino-oxyphenazine and the other bleaching bath containing thiourea, each of said baths exerting a different bleaching action on at least one and the same component image, thereby acceleratedly bleaching out dyestuff of at least one, but less than all, of the component images in at least one of said bleaching operations, and bleaching out dyestuff of from at least the remaining up to all of the component images in the other bleaching operation; and so adjusting the accelerated bleaching to the other bleaching as to yield a predetermined balance between the gradations of the color component images in the different layers.

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