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[54] **METHOD FOR PROCESSING BLACK-AND WHITE PHOTOGRAPHIC SILVER HALIDEMATERIAL**

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[58] **Field of Search** ..... 96/63, 66, 61, 50, 96/48 QP

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[57] **ABSTRACT**

A method for processing black-and-white negative photographic silver halide materials which comprises (a) developing the exposed black-and-wite photographic material, (b) bleaching said photographic material without oxidizing and dissolving the silver in a bleaching solution, and (c) subsequently developing said photographic material again with a black-and-white developer.

14 Claims, No Drawings

METHOD FOR PROCESSING BLACK-AND WHITE PHOTOGRAPHIC SILVER HALIDEMATERIAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of treating black-and-white negative photographic silver halide materials, and more particularly, it is concerned with a novel developing method which contains both a bleaching step and a second developing step between usual development process.

2. Description of Prior Art

In general, treatment of black-and-white negative photographic materials is carried out in the order of (1) development, (2) stopping, (3) fixing and (4) washing. Some light-sensitive materials, such as lithographic film, X-ray film, facsimile film (telephotographic film) and photographic plates for making an integral circuit require a high contrast and sufficient maximum density. For these purposes, various additives or developers having a special composition are used.

However, these treatment methods have not been satisfactory because they are also accompanied by some disadvantages, as mentioned hereinafter.

The disadvantages will now be illustrated, for example, with respect to a lithographic film. For the preparation of a screened dot image, a high contrast silver halide material generally called "lith film" is used. The original with continuous gradation is divided into a group of dots arranged in a network. That is to say, the density change is converted into an area change of dots and recorded on the lith film. Division into a dot group of a network is carried out by the use of a glass cross screen or contact screen. An image of the original is printed through such screen on a lith film or plate and then subjected to development, thus obtaining a dotted image. It is most preferable that such dot image consist of image spots having a maximum density and background having a minimum density, but formation of intermediate density zones called "fringe" around the dots is unavoidable since even a high contrast photographic light-sensitive material has an intermediate density or so-called half tone portion. The fringe tends to degrade the quality of a printed image and, accordingly, is not preferred in plate making. The less the fringe is, the better the quality of the dot image. Development of a lith film or lith plate is ordinarily carried out with an alkaline developer containing hydroquinone as a developing agent and an aldehyde-alkali metal bisulfite adduct, ascorbic acid and an acetone-bisulfite adduct as a preservative. In this developer, the concentration of free sulfite ion is low and thus the oxidized hydroquinone is not activated through formation of hydroquinonemonosulfonic acid. Rather a compound more active than hydroquinone is formed, thus causing a rapid and strong development. Even if this so-called lith development is carried out, complete elimination of the fringe around the dot is impossible.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a method for treating a black-and-white negative photographic material for forming a high contrast silver image.

It is another object of the present invention to provide a method for treating a black-and-white negative photographic material for obtaining a high developed density.

It is a further object of the present invention to provide a new treatment method for obtaining a dotted image, having an excellent dot quality, whereby fringes around dots are effectively removed.

These objects can be accomplished by developing an exposed black-and-white negative photographic silver halide material, and then subjecting it to a mild bleaching treatment and a second development.

The following embodiments are given in order to illustrate the invention in detail without limiting it:

Method I
1. lith development
2. stopping
3. bleaching
4. rinse
5. second development
6. stopping
7. fixing
8. water washing

Method II
1. lith development
2. bleaching
3. rinse
4. second development
5. stopping
6. fixing
7. water washing

Method III
1. lith development
2. bleaching
3. rinse
4. mono both development and fixing
5. water washing

Method IV
same as Method III except rinse step is omitted

As is evident from the above-mentioned embodiments, a method of treating black-and-white negative photographic materials according to this invention is characterized by the steps of bleaching and second development after the ordinary development.

DETAILED DESCRIPTION OF THE INVENTION

Methods II to IV are those which are more simplified than Method I. Their steps will now be illustrated, and in particular, with respect to a lith sensitive material. The lith development as the first step is similar to the ordinary lith development (so-called "infectious developer"), i.e., using a lith developer containing a developing agent, such as hydroquinone, a preservative such as a sodium bisulfite-paraformaldehyde adduct, ascorbic acid or kojic acid, an alkaline agent, such as sodium carbonate or caustic soda, and a fog inhibitor, such as potassium bromide or 1-phenyl-5-mercaptotetrazole. For example, Developer Super Lithodol (trademark, manufactured by Fuji Photo Film Co.) is a lith developer suitable for application in this invention.

When using a 1.5 percent aqueous solution of glacial acetic acid as a stopping bath, the lith development can be completely stopped for 10 seconds. As in Method II, the bleaching bath may hold another action as a stopping bath.

The bleaching bath contains an oxidizing agent and a halide compound, and if necessary, may contain an acid or an alkali as a pH regulator, another salt having

a buffering action and a further salt to raise the ionic strength.

As the oxidizing agent, there are used potassium or sodium bichromate, ferricyanide and sodium or ammonium persulfate, and as the halide compound, there are used sodium, potassium and ammonium chloride, bromide and iodide. In addition, an acid, such as acetic acid, hydrochloric acid or nitric acid, and a salt, such as sodium acetate or sodium hydrogen phosphate may be added. Bleaching time, depending upon the variety of a light-sensitive material as well as the composition of the bath, may range from 5 to 100 seconds, preferably 10 to 30 seconds. In this case, the bleaching solution must have a pH of no less than 1 to prevent the dissolution of silver.

The step of rinsing after the bleaching step may ordinarily be carried out by immersing in water for several seconds to 1 minute. Flowing water may be used or the rinsing step may be omitted as in usual IV without any substantial effects. 1–2 percent aqueous solutions of sodium sulfite may be used as a rinse solution. In any case, a suitable procedure may be taken as the occasion demands since this step serves to prevent the second developer from contamination of the bleaching solution so as to lengthen the effective life thereof.

The step of second development following the rinse step is not always carried out by the lith development, but the commonly used black-and-white developer may also be used. For example, commercial developers, such as Super Lithodol and other developers such as D-76, , D-72, D-8, FD-3, FD-31, D-85, FD-185, PM-MK and D-19 mentioned in "Kaguku Shashin Benran" II Ed., pages 58–67 (published by Maruzen Co.) may be used. In these developers there may be incorporated one or more developing agents,, such as metol(p-methylaminophenol sulfate), hydroquinone, 1-phenyl-3-pyrazolidone, 2,4-diaminophenol hydrochloride and N,N-diethyl-p-phenylenediamine, one or more of alkaline agents, such as sodium carbonate, caustic soda, trisodium phosphate, borax and potassium metaborate, one or more preservatives, such as sodium sulfite, ascorbic acid and hydroxylamine and other developing aids.

The second developer may be a mono-bath developing and fixing solution as mentioned in Method III. In this case, the subsequent processings are markedly simplified. The one-bath developing and fixing solution may be prepared by adding to the above-mentioned black-and-white developer one or more silver halide dissolving agents, such as sodium thiosulfate, potassium thiocyanate, ammonium thiosulfate, sodium thiocyanate and thioglycollic acid and adjusting suitably the pH and concentrations of the chemicals. The basic consideration of the composition thereof is disclosed by A. A. Newman in the *British Journal of Photography* 106, 44–48, 56, 66–68 (1959). The period of time for the second development is about 10 to 200 seconds, preferably 30–80 seconds in respect of the workability.

Following the second development, processings by the ordinary stopping bath and fixing bath are carried out in the case of Methods I and II, but the stopping bath may be omitted without any substantial effects.

The method of this invention is apparently similar to the method of treating a black-and-white reversal film, but in practice they are essentially different. In the case of the black-and-white reversal film, the steps of bleaching and second development are also carried out following the developing step. In this case, however, the bleaching solution used is a sulfuric and acetic acid acidic solution of potassium bichromate (pH: less than 1) which is much stronger than the bleaching solution of this invention and capable of oxidizing and dissolving the developed silver completely. The bleaching solution of this invention holds the developed silver forming a dot image as it is in the film. In the treatment of a reversal film, after the bleaching step, it is radiated by white light to form a latent image on an unexposed area, while in the method of the present invention, the radiation of white light is not carried out and, therefore, the unexposed area is not developed even in the second development; only the dot area is developed. This is a negative development.

The quality of a dot image according to this invention is improved so much that a sharp printing image may be given. In addition, the dot image correction operation called "dot etching," which is often carried out after development to improve the dot quality of screened negatives, is not required according to the method of the invention.

Another advantage of this invention is that it is possible to make thinner the thickness of an emulsion on a lith film or lith plate, thus saving the emulsion. The lith film or lith plate has an emulsion layer containing a relatively large amount of silver halide in order to raise sufficiently the blackened density of a dot image and to make the fringe as little as possible. Therefore, it is relatively expensive. The method of the invention can give such an excellent dot image quality that saving of silver halide is possible by thinning the emulsion layer or by decreasing the content of silver halide in the emulsion layer.

The method of this invention is applicable to treatment of any lith film or lith plate. It is applicable to any of silver chloride, silver bromide, silver chlorobromide and silver chloroiodobromide. Furthermore, it may be used irrespective of color sensitization, chemical sensitization and addition of a sensitizer, such as polyethylene glycol, or fog inhibitor, such as tetrazaindene and other additives.

The foregoing illustration is based on only a dot image photographic material, but the method of the invention is applicable to processing of X-ray photographic materials, facsimile films and photographic plates for making an integrated circuit, and other black-and-white negative photographic materials. The resulting image is hardened and highly densed. Of course, development may be carried out with an ordinary developer.

A better understanding of the present invention will be obtained from the following examples which are merely illustrative of the present invention and not limitative of such.

EXAMPLE 1

A commercial lith film was subjected to stepwise dot image exposure through a magenta contact screen of 133 lines and step wedge for sensitometry and then subjected to the following two developments for comparison:

Standard treatment (prior art method)		
developer I	20° C	3 minutes
stopping	20° C	15 seconds
fixing	20° C	3 minutes
water washing	20° C	5 minutes
Improved treatment (A)		
developer I	20° C	3 minutes
stopping	20° C	15 seconds

bleaching solution I	20° C	15 seconds
rinse	20° C	30 seconds
second development I	20° C	60 seconds
stopping	20° C	15 seconds
fixing	20° C	3 minutes
water washing	20° C	5 minutes

The compositions of the treating solutions are as follows:

Developer I	
water	500 ml
sodium sulfite	30 g
paraformaldehyde	7.5 g
potassium hydrogen sulfite	2.6 g
boric acid	7.5 g
hydroquinone	22.5 g
potassium bromide	1.6 g
water to 1000 ml	

Stopping solution

1.5% aqueous solution of glacial acetic acid

Fixing solution	
sodium thiosulfate	200 g
sodium sulfite	15 g
sodium acetate	10 g
glacial acetic acid	20 ml
phassium alum	15 g
water to 1000 ml	

Bleaching solution	
potassium bichromate	20 g
3% aqueous hydrochloric acid	50 ml
water to 1000 ml	

Second developer I

same as Developer I

The dot image samples treated by the above-mentioned two methods were traced by a microdensitometer to measure the extension of fringe around dots. The results are shown in Table 1, from which it is evident that the extension of fringe in the method of this invention is less than in the standard method. In this table, "Dot Area Ratio" means a ratio of the blackened parts of dots to a sample area and "Extension of Fringe" means a value of the size of a dot at a trace image density of 0.3 (diameter) minus the size at a density of 2.5.

TABLE 1

	Standard Treatment		Improved Treatment A	
Dot area ratio	20%	50%	20%	50%
Extension of fringe	28μ	30μ	12μ	12μ

EXAMPLE 2

A commercial lith film was exposed in a similar manner to that of Example 1 and then subjected to the following treatment:

Standard treatment

same as Example I

Improved treatment B

Bleaching solution II in place of Bleaching solution I of Improved treatment A

Bleaching solution II	
potassium bichromate	20 g
sodium chloride	30 g
glacial acetic acid	30 ml
water to 1000 ml	

Improved treatment C

Bleaching time is lengthened to 30 seconds in Improved treatment B

Improved treatment D

Bleaching solution III is used in place of Bleaching solution I in Improved treatment A

Bleaching Solution III	
ferricyanide	20 g
potassium bromide	15 g
water to 1000 ml	

Improved treatment E

Bleaching solution IV is used in place of Bleaching solution I of Improved treatment A

Bleaching solution IV	
ferricyanide	35 g
sodium chloride	65 g
water to 1000 ml	

Improved treatment F

Bleaching time is lengthened to 30 seconds in Improved treatment E

Improved treatment G

Bleaching solution V is used in place of Bleaching solution I in Improved treatment A

Bleaching solution V	
ferricyanide	35 g
sodium chloride	60 g
glacial acetic acid	60 ml
water to 1000 ml	

The results are shown in Table 2, from which it is evident that the extension of fringe in the method of this invention is markedly reduced as compared with the prior art method.

TABLE 2

Treatment Method		Extension of fringe at a dot area ratio of 50%
Standard (prior art)		30μ
Improved treatment:	B	10μ
	C	7μ
	D	7μ
	E	8μ
	F	5μ
	G	3μ

EXAMPLE 3

A commercial lith film was exposed in a similar manner to that of Example 1 and then subjected to the following treatments:

Improved treatment H		
Developer I	20° C	3 minutes
Stopping	20° C	15 seconds
Bleaching solution VI	20° C	30 seconds
Rinse	20° C	30 seconds
Second developer II	20° C	90 seconds
Water washing	20° C	5 minutes

The compositions of the treating solutions are as follows:

Bleaching solution VI	
potassium bichromate	20 g
3% aqueous solution of hydrochloric acid	150 ml
water to 1000 ml	

Second developer II

The following compounds are added per 1000 ml of Developer I:

addition salt of formaldehyde and sodium sulfite	35 g
caustic soda	5 g
1-phenyl-5-mercaptotetrazol	0.1 g
methanol	10 ml
potassium thiocyanate	100 g

Improved treatment I

same as Improved treatment H except using Bleaching solution V in place of Bleaching solution VI in Improved treatment H

Improved treatment J

Second developer in Improved treatment H is substituted by the following Second developer III

Second Developer III

Potassium thiocyanate of Second developer II is converted into 70 g/l of sodium thiosulfate

As is evident from the results shown in Table 3, the effects of the invention can be attained even if the processings after the second development are simplified by a one-bath developing and fixing solution.

TABLE 3

Treatment Conditions		Extension of fringe at an area ratio of 50%
Standard treatment		30μ
Improved treatment:	H	7μ
	I	10μ
	J	18μ

EXAMPLE 4

A support member was coated with each of silver chloride, silver bromide and silver chlorobromide (silver chloride 70 mol percent) to prepare a photographic film, which was then subjected to dot image photographing in a similar manner to that of Example 1 and Standard treatment of the prior art and Improved treatment K.

Improved treatment K		
Developer II	20° C	165 seconds
Bleaching solution V	20° C	30 seconds
Second developer Iv	20° C	120 seconds
water washing	20° C	5 minutes
Developer II		
hydroquinone		20 g
sodium sulfite		2 g
formaldehyde and sodium bisulfite adduct		50 g
sodium carbonate monohydrate		80 g
boric acid		7 g
potassium bromide		2 g
water to 1000 ml		
Second developer II		
1-phenyl-5-mercaptotetrazole		0.1 g
potassium thiocyanate		100 g
are added per 1000 ml of Developer II		

Extension of the fringe of dot was reduced by the method of the invention as shown in Table 4.

TABLE 4

	Extension of fringe at a dot area ratio of 50%	
Sample	Standard treatment	Improved treatment L
silver chloride emulsion	28	9
silver bromide emulsion	35	10
silver chlorobromide emulsion	23	8

EXAMPLE 5

A film was coated with an emulsion consisting of silver chlorobromide containing 70 mol % silver chloride and gelatin having a silver chlorobromide to gelatin ratio by weight of 1:1.3 so as to vary the coating thickness thus obtaining three kinds of lith films, A, B and C:

A coated silver amount 51 mg Ag/dm²

B coated silver amount 42 mg Ag/dm²

C coated silver amount 32 mg Ag/dm²

Sample A has a coated silver amount necessary for the ordinary lith film but the coated silver amount of Samples B and C is not sufficient to give a dot image quality by the known lith developing method.

When each sample was subjected to dot image exposure and to Improved treatment F, a very excellent dot image quality was obtained and the extension of fringe was: Sample A 5μ, B 5μ and C 6μ. When it was subjected to Standard treatment of the prior art, on the other hand, the extension of fringe was: A 20μ, B 23μ, and C 26μ. Accordingly, samples of low silver emulsion could be used as a lith film by application of the method of this invention.

EXAMPLE 6

When Improved treatment G was used in place of Improved treatment F in Example 5, the extension of fringe was: Sample A 3μ, B 3μ, and C 3μ.

EXAMPLE 7

When Improved treatment H was used in place of Improved treatment F in Example 5, the extension of fringe was: Sample A 7μ, B 7μ and C 8μ.

EXAMPLE 8

A film base was coated with a silver iodobromide gelatin emulsion (silver iodide 5 mol percent) so as to give a coated silver amount of 40 mg/dm² to thus obtain a light-sensitive material for X-rays, which was then subjected to sensitometric exposure and to the following treatment:

	Prior art method	Method of invention
development	34° C 60 seconds	same as prior art
rinse	34° C 30 seconds	same as prior art
fixing	34° C 90 seconds	
water washing	34° C 60 seconds	
bleaching		34° C 40 seconds
rinse		34° C 10 seconds
redevelopment		34° C 150 seconds
water washing		34° C 60 seconds

A commercial developer for X-ray films (Rendol manufactured by Fuji Photo Film Co.) was used as a developer. The bleaching solution was prepared according to the foregoing formula VI and the following mono-bath developing and fixing solution was used for the redevelopment:

caustic soda	32 g
sodium sulfite	83 g
1-phenyl-3-pyrazolidone	6.7 g
hydroquinone	58 g
sodium thiosulfate	92 g
potassium iodide	0.3 g
water to 1000 ml	

The sample treated by the method of this invention gave an increase of 50 percent to the sensitivity represented by the reciprocal of exposure quantity giving a density of above 0.2 fog, as compared with that treated by the prior art method. The gamma was increased by 0.3. Moreover, increase of fog could be suppressed to 0.03 as compared with 0.09 of the prior art method.

EXAMPLE 9

A superfine grain and high resolving power dry plate of silver chlorobromide was subjected to sensitometric exposure and to the following treatment:

	Prior art method	Method of invention
Development	20° C 5 minutes	same as prior art
Fixing	20° C 1 minute	same as prior art
Stopping	20° C 1 minute	
Water washing	20° C 2 minutes	
Bleaching		20° C 20 seconds
Rinse		20° C 20 seconds
Redevelopment		20° C 3 minutes
Stopping		20° C 1 minute

Fixing	20° C 1 minute
Water washing	20° C 1 minute

A developer according to D-19 recipe ("Kagaku Shashin Benran" II Ed., published by Maruzen Co.) was used and the ordinary stopping and fixing solutions were used. Three kinds of bleaching solutions according to the foregoing formulas I, VI and III were used and Developer D-19 was reused for the redevelopment.

The results are shown in the following table, from which it is evident that an excellent hardening effect can be obtained by the method of the present invention:

	Relative sensitivity	Gradation (Gamma)
Prior art method	100	2.5
Bleaching solution I	150	3.6
Bleaching solution VI	140	4.5
Bleaching solution III	140	3.4

Although the present invention has been adequately set forth in the foregoing specification and examples included therein, it is readily apparent that various changes and modifications can be made without departing from the scope and spirit thereof.

We claim:

1. A method for treating an exposed black-and-white negative photographic silver halide material to obtain a high contrast silver image, wherein the chloride content of said silver halide material is present in an amount of at least 70 mol percent, which comprises:

a. developing the exposed black-and-white photographic material,

b. bleaching said photographic material without oxidizing and dissolving the silver in a bleaching solution having a pH of at least 1, and

c. subsequently, negative-developing said photographic material for a second time with a black-and-white developer.

2. The method of claim **1**, wherein the first development step is carried out with a developer containing hydroquinone and a sodium sulfite-paraformaldehyde adduct.

3. The method of claim **2**, wherein said developer further contains at least one member selected from the group consisting of ascorbic acid and sodium sulfite.

4. The method of claim **1**, wherein said bleaching solution contains an oxidizing agent and a halide.

5. A method for treating an exposed black-and-white negative photographic material to obtain a high contrast silver image, wherein the chloride content of said silver halide material is present in an amount of at least 70 percent, which comprises the steps of:

a. developing,

b. stopping,

c. bleaching at a pH of at least 1,

d. rinsing,

e. negative-developing,

f. stopping,

g. fixing, and

h. washing.

6. A method for treating an exposed black-and-white negative photographic material to obtain a high contrast silver image, wherein the chloride content of said silver halide material is present in an amount of at least 70 mol percent, which comprises the steps of:

a. developing,

b. bleaching at a pH of at least 1,

c. rinsing,

d. negative-developing,

e. stopping,

f. fixing, and

g. washing.

7. A method for treating an exposed black-and-white negative photographic material to obtain a high contrast silver image, wherein the chloride content of said silver halide material is present in an amount of at least 70 mol percent, which comprises the steps of:

a. developing,

b. bleaching at a pH of at least 1,

c. rinsing

d. mono-bath negative-developing and fixing, and

e. washing.

8. A method for treating an exposed black-and-white negative photographic material to obtain a high contrast silver image, wherein the chloride content of said silver halide material is present in an amount of at least 70 mol percent, which comprises the steps of:

a. developing,

b. bleaching at a pH of at least 1,

c. mono-bath negative-developing and fixing, and

d. washing.

9. The method of claim **1**, wherein said bleaching step is carried out over a period of from 5 to 100 seconds.

10. The method of claim **1**, wherein said bleaching step is carried out over a period of from 10 to 30 seconds.

11. The method of claim **1**, wherein said second developing step is carried out over a period of from 10 to 200 seconds.

12. The method of claim **1**, wherein said second developing step is carried out over a period of from 30 to 80 seconds.

13. The method of claim **1**, further comprising at least one stopping, rinsing and washing step conducted after treating steps (a) through (c).

14. The method of claim **1**, further comprising a fixing step, which step takes place either during or after step (c).

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