

## 1

3,578,454

## COLOR PHOTOGRAPHIC PROCESSING

Hiroyuki Amano, Reiichi Ohi, Haruhiko Iwano, and Kazuo Shirasu, Kanagawa, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Kanagawa, Japan  
 No Drawing. Filed Dec. 13, 1967, Ser. No. 690,068  
 Claims priority, application Japan, Dec. 14, 1966,  
 41/81,967

Int. Cl. G03c 5/32, 5/38

U.S. CL. 96—60

12 Claims

## ABSTRACT OF THE DISCLOSURE

A method of color processing for a photographic light-sensitive color element comprising, at least, development, stop-fixing, and bleach-fixing, the improvement which comprising processing the light-sensitive element in a bath containing a water-soluble iron complex salt and a compound represented by the general formula:



wherein A represents an alkylene group having from 2 to 4 carbon atoms and n is a positive integer, the bath being a bleach-fixing bath or a separate bath in which the element is processed, after color development, but no later than bleach-fixing.

## BACKGROUND OF THE INVENTION

## (1) Field of the invention

The present invention relates to color photographic processing and more particularly to a bleaching process for color development, and to such a process using a solution containing a specific compound.

## (2) Description of the prior art

The procedures of color development processes generally include a color development, stop-fixing, bleaching (de-silvering), fix-cleaning, hardening, stabilizing and some additional processings. Each of the baths used in these processings has its own composition fitted to its purpose.

Typical bleaching solutions for color development processing contain potassium ferricyanide or a water-soluble iron complex salt, such as,  $\text{Fe}^{3+}$ -ethylenediaminetetraacetic acid complex.

In the case of using potassium ferricyanide, the solution has enough ability to bleach developed silver, therefore the degradation in image quality caused by insufficient bleaching will not occur. However, when potassium ferricyanide is present together with a thiosulfate which is used as a fixing agent, the thiosulfate will be decomposed by potassium ferricyanide because of its high oxidizing power; that is, the bleaching solution containing ferricyanide has the disadvantage that the bleaching bath must be separated from the fixing bath, which prolongs the process considerably. Furthermore, there is also another disadvantage in that potassium ferricyanide is unstable in the solution and tends to be converted into potassium ferricyanide.

On the other hand, a water-soluble iron complex salt, such as  $\text{Fe}^{3+}$ -ethylenediaminetetraacetic acid complex, can exist stably even in the presence of a thiosulfate. Therefore, simultaneous bleaching and fixing in one bath (blixing) is possible. However, the bleaching power of the bleach-fixing bath containing an iron complex salt and a thiosulfate is not sufficient. Hence, various bleach-

## 2

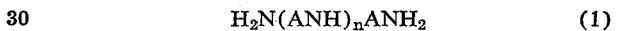
ing accelerators have been investigated to increase the bleaching power of the bath (e.g., German Patent 1,127,715), but an additive with sufficient accelerating power has not yet been discovered.

5 As an example of a bleaching accelerator, it has been known to incorporate thiourea or thiourea derivatives in bleach-fixing baths but the incorporation in the bleach-fixing bath is accompanied by faults, such as, the contamination of the bleach-fixing solution with color developing solution causing considerable increase in color fog.

10 Therefore, an object of the present invention is to provide a color development process having a sufficient bleaching power and providing no color fog. Another 15 object of this invention is to provide a color development process using a bleach-fixing solution containing a water-soluble iron complex salt having sufficient bleaching power and giving no color fog. Still another object of the present invention is to provide a color development process able 20 to give a good colored image by applying bleach-fixing directly after color development without applying stop-fixing.

## SUMMARY OF THE INVENTION

25 The inventors have studied ways to attain the aforesaid objects and as a result, it has been found that these objects are achieved by the incorporation in a bleach-fixing bath of the color photography compound represented by the general formula



wherein A represents an alkylene group having 2-4 carbon atoms, and n is a positive integer. This additive markedly increases the bleaching power of the bath and also improves the color fog preventing effect. Moreover, in regard 35 to the bleaching accelerator effect, the aforesaid compound may be effectively added to the stop-bleaching bath or a bath between the stop-bleaching bath and the bleach-fixing bath. In another aspect, that is, in regard 40 to the prevention of color fog, the aforesaid compound may very effectively be added to a bath between the color developer and the stop-fixing bath, to the stop-fixing bath, or to the bath between a stop-fixing bath and a bleach-fixing bath.

45 In the case of conventional color photographic processing, if a stopper or a stop-fixing bath is omitted and the photographic elements are bleach-fixed (blixed) directly after color development, there occurs color fog which is considered to be caused by the color developer which 50 remains in the emulsion layers. Hence, in practice, the stop-fixing process cannot be neglected in conventional processing systems. On the other hand, incorporation of compound (1) mentioned above in a processing bath between the color development and the bleach-fixing or in 55 the bleach-fixing bath, according to the present invention, sufficiently prevents the formation of color fog. Hence, the stop-fixing bath is not always necessary.

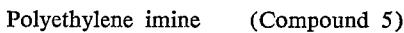
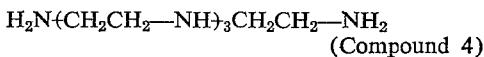
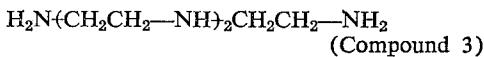
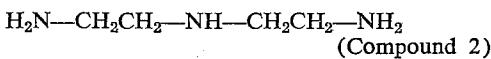
Now, it is known that some of the compounds (1) are 60 reported to be a kind of reduction sensitizer for silver halide emulsions (e.g., U.S. Patent 2,518,698), but when the compound is used in the amount employed in the known art, or is added to emulsions during the preparation thereof, neither the bleaching promoting effect, nor the color fog preventing effect of this invention can be obtained.

## DETAILED DESCRIPTION OF THE INVENTION

Typical examples of compounds used in the present invention expressed by the aforesaid general Formula

## 3

1 are as follows: However, the invention is, of course, not limited only to them.



Compound 5 is a compound represented by the formula:



and is available commercially under the trade name Sumirez Resin P (average polymerization degree  $\gamma$ =about 100 made by Somitomo Chemical Industries Co. Ltd., in Japan.

In addition, the amount of the aforesaid composition added to the processing solution is generally 0.3 g./liter to 50 g./liter preferably 2 g./liter to 10 g./liter. Since the compound of this invention is alkaline, the pH of the bleach-fixing bath must be adjusted to 6.4-7.1.

The aforesaid compounds may be used alone or as a combination of two or more of them.

Now, the invention will be described by the following examples wherein the bleach-promoting effect and the color fog preventing effect of the aforesaid compounds are illustrated. However, it should be understood that the invention is not limited to these examples.

Example 1.—Into one liter of a bleach-fixing bath of the following composition was added 10 g. of each of aforesaid Compounds 1-5.

	G.
Iron salt of ethylenediaminetetraacetic acid	34
Boric acid	45
Sodium thiosulfate	140
Additive	10
Water to make 1000 ml.	
pH 6.8±0.2.	

The control bleach-fixing bath for comparison had the following composition:

	G.
Iron salt of ethylenediaminetetraacetic acid	34
Sodium carbonate (mono-hydrate)	11
Boric acid	45
Sodium thiosulfate	140
Water to make 1000 ml.	
pH 6.8±0.2.	

An exposed color print paper was color developed, stop-fixed, then processed in the bleach-fixing bath of the above formula and the time needed for bleaching was determined. The results are shown below.

Additive:	Time (minutes)
Compound 1	2
Compound 2	2
Compound 3	2
Compound 4	2
Compound 5	2
None	6

As is clear from the above table, it was confirmed that the addition of Compounds 1 to Compound 5 had very excellent bleach promoting effect. The processing temperature in the experiments was 24° C.

When color films were processed instead of color print papers, almost the same results were obtained.

Example 2.—An aqueous solution of 2 g./liter of each of the Compounds 1 to 5 of this invention was prepared. A color print paper was exposed, processed in a development bath and in a stop-fixing bath, then immersed for

75

## 4

2 minutes in the aqueous solution thus prepared and then bleach-fixed. The time required for completion of the bleaching was measured in each case including a control experiment in which the aqueous solution was not used. The results are shown below.

Additive:	Time (minutes)
Compound 1	5
Compound 2	5
Compound 3	5
Compound 4	5
Compound 5	5
Compound 6	6

As is clear from the experimental results, it was confirmed that in the case of employing an aqueous solution of the compound of this invention, the bleach-accelerating effect in the subsequent bleach-fixing bath was excellent.

Further, the stains of the samples processed by the aqueous solution of the compound of the present invention were compared with the stains of a sample which was not processed by the aqueous solution. The results are shown in the following table.

Stain	Compound					Control
	1	2	3	4	5	
Yellow stain	0.10	0.10	0.10	0.10	0.10	0.25
Magenta stain	0.10	0.10	0.10	0.10	0.10	0.18
Cyan stain	0.08	0.08	0.08	0.08	0.08	0.21

As is clear from the experimental results, the formation of stains on the color print was markedly reduced by the aqueous solution of the compound of this invention. The processing temperature in these experiments was 24° C.

When color films were processed, almost the same results were obtained.

Example 3.—After exposure and color development, a color print paper was directly immersed in the bleach-fixing bath prepared in Example 1 for 3 minutes without processing in a stopping bath or stop-fixing bath. As a control experiment, the same color print paper was immersed for 3 minutes in a bleach-fixing bath containing no compound of this invention under the same conditions. The formation of stains was compared in both cases, the results of which are shown in the following table, in which each stain was shown by three color densities.

Stain	Compound					Control
	1	2	3	4	5	
Yellow stain	0.16	0.16	0.16	0.16	0.16	0.45
Magenta stain	0.13	0.13	0.13	0.13	0.13	0.30
Cyan stain	0.12	0.12	0.12	0.12	0.12	0.35

As is clear from the results, Compounds 1-5 of this invention showed very excellent stain preventing effect.

In these experiments, the developed silver on the color print paper was completely bleached in 3 minutes of blixing by the bath containing the compound of this invention, whereas the developed silver was not completely bleached in the case of the bath containing no compounds of this invention. The processing temperature in these experiments was 24° C. When color films were processed as above, almost the same results were obtained.

What is claimed is:

1. In a method of color processing a photographic light-sensitive color element comprising image-wise exposing the element, developing the exposed element by a developer capable of forming a silver and a color image and bleach-fixing the developed element to remove the silver image, the improvement which comprises processing the color element after development in a bleach-fixing bath containing a water-soluble iron complex salt and an amine compound represented by the general formula:



## 5

wherein A represents an alkylene group having from 2 to 4 carbon atoms and n is 0 or a positive integer, the amount of said amine compound being from about 0.3 g. to about 50 g. per one liter of the bleach-fixing bath.

2. The method of color processing as claimed in claim 1 wherein said amine compound is selected from the group consisting of  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ,



$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2-\text{NH})_3\text{CH}_2\text{CH}_2-\text{NH}_2$ , and polyethylene-imine.

3. The method of color processing as claimed in claim 1 wherein said water-soluble iron complex salt is the iron salt  $\text{Fe}^{3+}$ -ethylenediamine-tetraacetic acid.

4. The method of claim 1 wherein from 2 g. to 10 g. of said amine compound are present per liter.

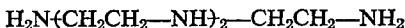
5. The method of claim 1 wherein the pH of the bleach-fixing bath is from 6.4 to 7.1.

6. In a method of color processing a photographic light-sensitive color element comprising image-wise exposing the element, developing the exposed element by a developer capable of forming a silver and a color image and bleach-fixing the developed element to remove the silver image, the improvement which comprises processing the color element after development but prior to bleach-fixing in a bath containing an amine compound represented by the general formula:



wherein A represents an alkylene group having from 2 to 4 carbon atoms and n is 0 or a positive integer, and subsequently bleach-fixing said color element in a bleach-fixing bath containing a water-soluble iron complex salt, the amount of said amine compound in said bath being from about 0.3 g. to about 50 g. per one liter of said bath.

7. The method of color processing as claimed in claim 6 wherein said compound is selected from the group consisting of  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ,



$\text{H}_2\text{N}(\text{CH}_2\text{CH}_2-\text{NH})_3\text{CH}_2\text{CH}_2-\text{NH}_2$ , and polyethylene-imine.

## 6

8. The method of color processing as claimed in claim 6 wherein said water-soluble iron complex salt is the iron salt  $\text{Fe}^{3+}$ -ethylenediamine-tetraacetic acid.

9. The method of claim 6 wherein from 2 g. to 10 g. of said amine compound are present per liter.

10. The method of claim 6 wherein the pH of the bleach-fixing bath is from 6.4 to 7.1.

11. The method of claim 6 wherein the bath in which said amine compound is present is a stop-bleaching bath.

12. The method of claim 6 wherein the processing of said color element after color development includes a stop-bleaching bath prior to processing in said bleach-fixing bath, and said amine compound is present in a bath between said stop-bleaching bath and said bleach-fixing bath.

## References Cited

## UNITED STATES PATENTS

20	2,310,981	2/1943	Meschter	96-22
	2,322,084	6/1943	Young et al.	96-53
	2,706,687	4/1955	Rees et al.	96-61X
	2,857,275	10/1958	Land et al.	96-61X
25	3,141,771	7/1964	Bard et al.	96-22
	3,168,400	2/1965	Blackmer et al.	96-22
	3,169,992	2/1965	Henn	96-61X
	3,256,092	6/1966	Means et al.	96-60
	2,827,375	3/1958	Andreyev	96-62X
30	3,259,497	7/1966	Wartburg	96-60X
	3,271,153	9/1966	Miller et al.	96-61
	3,352,676	11/1967	Morcher et al.	96-22X
	3,372,030	3/1968	Jacobson	96-60UX

## FOREIGN PATENTS

35	739,202	10/1955	Great Britain	96-60
	717,018	8/1965	Canada	96-60

WILLIAM D. MARTIN, Primary Examiner

40 H. J. GWINNELL, Assistant Examiner

U.S. CL. X.R.

96-61

45