United States Patent

Willems

[15] **3,658,535**

[45] **Apr. 25, 1972**

[54] PHOTOGRAPHY

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[22] Filed: **Nov. 27, 1968**

[21] Appl. No.: **779,656**

[30] **Foreign Application Priority Data**

Dec. 27, 1967 Great Britain 58,656/67

[52] **U.S. Cl.** **96/59**, 96/60, 96/64

[51] **Int. Cl.** **G03c 5/50**, G03c 5/32

[58] **Field of Search** 96/60, 64, 66, 66.5, 10, 59

[56] **References Cited**

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3,300,306	1/1967	Seven	96/66
3,256,092	6/1966	Means et al.	96/60
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Robert L. Smith The Sequestration of Metals MacMillan (1959)

Primary Examiner—William D. Martin
Assistant Examiner—M. Sofocleous
Attorney—Alfred W. Breiner

[57] **ABSTRACT**

The method of rendering silver halides developable in photographic elements by treating the elements with a processing liquid comprising a tin(II)chelate of a (poly)amino(poly)carboxylic acid in acid form or in the form of a water-soluble salt is described. The aforesaid tin(II)chelates have good chemical fogging action forming developable specks in a light-sensitive silver halide material and remain stable in alkaline solutions permitting their incorporation in a developer solution eliminating need of an independent processing bath.

30 Claims, No Drawings

PHOTOGRAPHY

This invention relates to photographic processing liquids for the treatment of light-sensitive silver halide materials and to methods for the production of images wherein such processing liquids are used.

It is known to produce a black-and-white positive image of an original by developing an exposed photographic silver halide emulsion, bleaching and clearing the developed emulsion and then developing all or part of the residual image-wise distributed silver halide. In color processes, the exposed emulsions may be first developed in a black-and-white developer, then the residual silver halide is color developed. In either case, the photographic element having in a layer an image-wise distribution of silver halide may be rendered developable by an overall exposure to light or by treatment with chemical fogging means prior to the second development.

It is an object of the present invention to provide chemical fogging agents novel for the purpose of rendering a layer comprising an image-wise distribution of silver halide developable, i.e., forming developable specks in said layer.

Another object of the present invention is to provide processing liquids amongst others photographic black-and-white as well as color developers containing said novel fogging agents.

A further object of the present invention is to provide a process for rendering developable silver halides in photographic elements by treating said elements with the said processing liquids.

A still further object of the present invention is to provide processes of producing a photographic reversal or direct positive black-and-white or color image in which processes use is made of processing liquids containing said novel fogging agents.

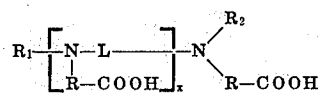
These objects and other objects, which will become apparent from the description below, are accomplished by the use as chemical fogging means of tin(II)chelates of (poly)amino-(poly)carboxylic acids in acid form or in the form of a water-soluble salt.

The tin(II) chelates of (poly)amino-(poly)-carboxylic acids apart from having a good fogging action to form developable specks in light-sensitive silver halide material when the latter is treated with an aqueous solution comprising a said tin(II)chelate are also characterized by remaining stable in alkaline solutions so that they can be incorporated in the second photographic developer solution itself and that no independent processing bath is necessary.

The tin(II) chelates of (poly)amino-(poly)carboxylic acids of use as chemical fogging means according to the invention are more particularly the tin(II)chelates obtained by reaction of water-soluble tin(II)salts (chloride, acetate, nitrate, sulphate, etc.) with (poly)amino-(poly)carboxylic acid sequestering compounds or water-soluble salts thereof.

Examples of suitable (poly)amino-(poly)carboxylic acid sequestering compounds for reaction with tin(II) salts to form the corresponding tin(II) chelates as well as details about the preparation of said sequestering compounds can be found in Ind.Chim.Belg. Tome XXI (1956) pp. 338–346 and in Ind.Chim.Belg. Tome XXIII (1958) pp. 1,105–1,115.

Particularly suitable (poly)amino-(poly)carboxylic acids for forming in acid or salt form with the tin(II) salts the corresponding tin(II) chelates can be represented by the following non-limitative general formula :



wherein :

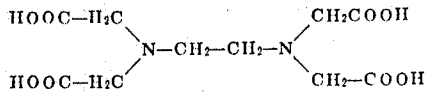
L stands for alkylene including substituted alkylene, e.g., hydroxy-alkylene, cycloalkylene including substituted cycloalkylene or alkylene interrupted by one or more hetero atoms, such as an oxygen atom,

x represents 0, 1 or 2,

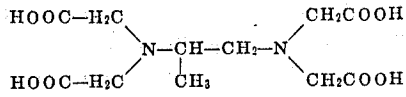
R stands for lower alkylene, e.g., methylene and ethylene including substituted lower alkylene, e.g., alkylene substituted by alkyl, aryl, aralkyl, including substituted alkyl, aryl and aralkyl, and

each of R_1 and R_2 (the same or different) stands for hydrogen, lower alkyl including substituted lower alkyl, aralkyl, including substituted aralkyl or aryl including substituted aryl; examples of substituted alkyl groups for R_1 and for R_2 are alkyl substituted with hydroxyl, halogen, alkoxy, carbamoyl, amino, substituted amino, e.g., dihydroxy-alkylamino, epoxy, carboxyl, sulpho, phosphono, mercapto, alkylmercapto, alkoxycarbonyl, a nitrogen-containing heterocyclic ring, e.g., pyridyl and examples of substituted aryl groups and aralkyl groups for R_1 and/or R_2 are : aryl and aralkyl substituted by hydroxyl, halogen, alkyl, alkoxy, nitro, carboxyl and sulpho.

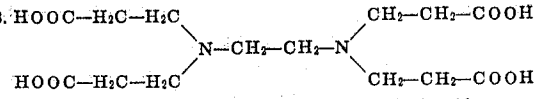
The following is a non-limitative list of examples of (poly)amino-(poly)carboxylic acids corresponding to the above general formula :

1. 

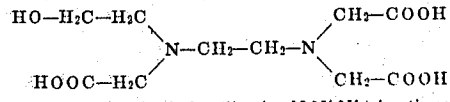
ethylenediamine,N,N,N′,N′-tetraacetic acid

2. 

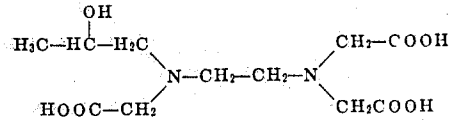
1,2-propylenediamine,N,N,N′,N′-tetraacetic acid

3. 

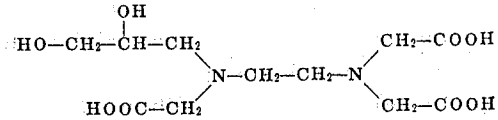
ethylenediamine,N,N,N′,N′-tetrapropionic acid

4. 

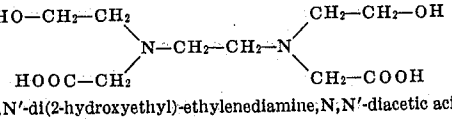
N-(2-hydroxyethyl)-ethylenediamine,N,N′,N′-triacetic acid

5. 

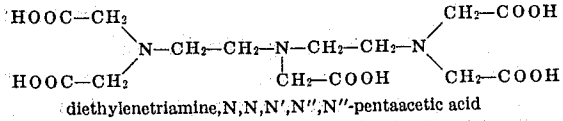
N-(2-hydroxypropyl)-ethylenediamine,N,N′,N′-triacetic acid

6. 

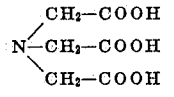
N-(2,3-dihydroxypropyl)-ethylenediamine,N,N′,N′-triacetic acid

7. 

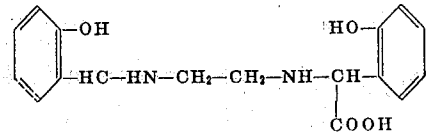
N,N′-di(2-hydroxyethyl)-ethylenediamine,N,N′-diacetic acid

8. 

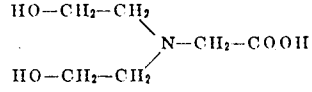
diethylenetriamine,N,N,N′,N″,N″-pentaacetic acid

9. 

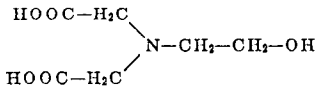
nitrilo triacetic acid

10. 

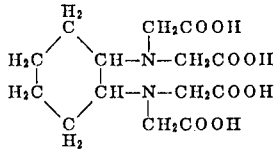
ethylenediamine,N,N'-di-(o-hydroxyphenyl acetic acid)

11. 

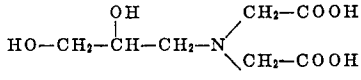
di(2-hydroxyethyl)amino acetic acid

12. 

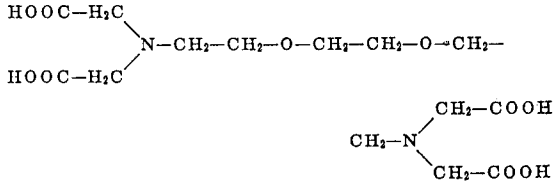
2-hydroxyethyl-amino diacetic acid

13. 

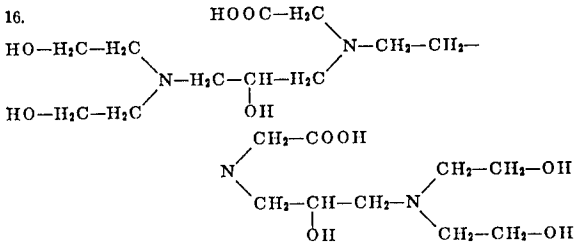
1,2-aminocyclohexane,N,N,N',N'-tetraacetic acid

14. 

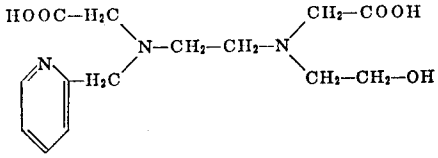
2,3-dihydroxypropyl-aminodiacetic acid

15. 

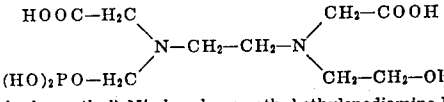
ethyleneglycol bis(2-aminoethyl),N,N,N',N'-tetraacetic acid

16. 

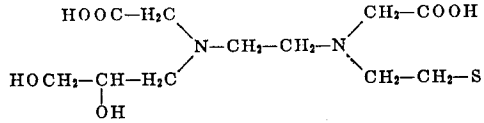
N,N'-di[3-di(2-hydroxyethyl)-amino-2-hydroxy-porpyl]-ethylenediamine, N,N'-diacetic acid

17. 

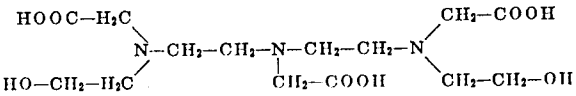
N-(2-hydroxyethyl)-N'-(α-pyridinomethyl)-ethylenediamine,N,N'-diacetic acid

18. 

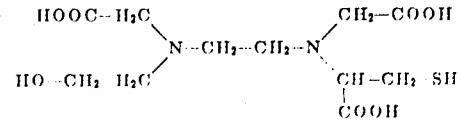
N-(2-hydroxyethyl)-N'-phosphonomethyl-ethylenediamine,N,N'-diacetic acid

19. 

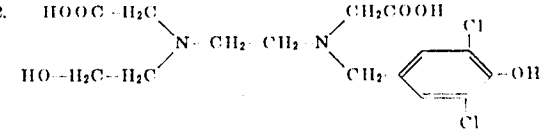
N-(2,3-dihydroxypropyl)-N'-(2-sulphoethyl)-ethylenediamine,N,N'-diacetic acid

20. 

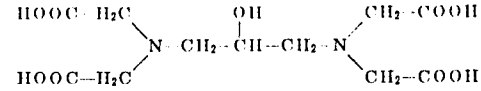
N,N'-di(2-hydroxyethyl)-ethylenetriamine,N,N'-N''-triacetic acid

21. 

N-(2-mercapto-1-carboxy-ethyl)-N'-(2-hydroxyethyl)-ethylenediamine, N,N'-diacetic acid

22. 

N-(3,5-dichloro-4-hydroxy-benzyl)-N'-(2-hydroxy-ethyl)-ethylenediamine N,N'-diacetic acid

23. 

2-hydroxy-propylenediamine,N,N,N'-N'-tetraacetic acid

The process of the invention for the production of a reversal black-and-white image in a light-sensitive silver halide emulsion layer comprise the consecutive steps of image-wise exposing said layer, developing the exposed silver halide material in an ordinary photographic black-and-white developer, eliminating the developed silver image, e.g., in an ordinary photographic bleaching bath containing an oxidizing agent such as potassium dichromate, and developing the remaining unexposed silver halide in a black-and-white developer rendered developable by the presence in the processing liquid for the latter development of a tin(II) chelate as referred to above and/or by the presence of a said tin(II) chelate in another processing liquid with which the light-sensitive material is wetted after the first development and before the last development.

In the process of the invention for the production of a reversal color image in a photographic element the second development is a color development with a color developing agent which undergoes a coupling reaction with a color coupler, which can be present either in the color developer itself or most advantageously in the photographic element.

The said process for the production of a reversal color image comprises the consecutive steps of image-wise exposing a light-sensitive silver halide material, developing the exposed silver halide in a black-and-white developer, developing the residual unexposed silver halide with a color developer in the presence of a color coupler, said residual silver halide being rendered developable by the presence in the color developer and/or in a processing liquid, with which the photographic material is wetted before the color development and after the black-and-white development, of a tin(II) chelate as referred to above, and finally eliminating the developed silver.

In order to stabilize the photographic direct positive image obtained the material is generally fixed, e.g., in a usual fixing solution such as a thiosulphate solution and washed, whereupon the said material may be dried or glazed.

For the production of reversal color images in multilayer photographic color materials, which normally contain in three silver halide emulsion layers, selectively sensitive to blue, green and red light non-migratory color couplers for yellow, magenta and cyan respectively, the said material is first image-wise exposed to a colored subject, and then black-and-white developed whereupon treatment with a tin(II) chelate solution as aforesaid follows prior to or simultaneously with treatment with a color developer.

It is also possible that the color couplers are not incorporated in the differently sensitized silver halide emulsion layers of a photographic multilayer color material and that each layer should be separately developed in a color developer comprising the appropriate color coupler. Normally, for the production of reversal color images in suchlike material the color development of each layer is preceded by a selective re-exposure step. The chemical fogging agents of the present invention can be used in suchlike processes for

rendering residual silver halide developable only in lieu of the last re-exposure step, i.e., prior to or simultaneously with the last color development step since the said tin(II)chelates when used immediately after the black-and-white development would render all residual silver halide developable and no selective color formation would be effected. Thus, the treatment with the said tin(II) chelates could be advantageously applied in lieu of the re-exposure of the third layer, particularly because said third re-exposure often presents difficulties. Indeed, since the silver halide emulsion layers have already undergone extensive treatment and development in alkaline solutions, the remaining silver halide would be inadequately exposed during the last re-exposure, or the sensitizing dyes and other emulsion addenda would be diminished in effectiveness by the extensive processing.

Color development can be carried out using any of the well known developing agents that are capable of coupling in oxidized form with the color couplers. Particularly useful color developing agents are aromatic amine compounds for example the phenylene diamines and derivatives thereof, e.g., the N,N-dialkyl-p-phenylene diamines such as N,N-diethyl-p-phenylene, N,N-diethyl-2-methyl-p-phenylene diamine, N,N-dialkyl-N'-sulphomethyl-p-phenylene diamines and N,N-dialkyl-N'-carboxymethyl-p-phenylene diamines.

The chemical fogging agents according to the present invention can also be successfully applied in the preparation of photographic color images according to the so-called silver dye bleach process.

In the silver dye bleach process for producing a multicolour image a multilayer photographic element is used which normally comprises three silver halide emulsion layers selectively sensitive to blue, green and red light said emulsion layers being dyed with yellow, magenta and cyan dyes particularly azo dyes. On black-and-white development of said material a negative silver image is formed and the dyed layers are then treated with a bleaching solution (a silver-dye bleach) in order to eliminate the developed silver image as well as the azo-dye in correspondence with said silver image which results in the formation of a positive color image.

By black-and-white reversal processing as described above of a photographic element for use according to the silver dye bleach process followed by silver dye bleaching, a negative color image of the original can be formed so that when the original is a color negative a color positive can be obtained therefrom.

With the fogging agents according to the present invention images of good quality are obtained, i.e., a quality at least as good as that of images obtained in processes where instead of chemical fogging means an overall exposure step is used.

The tin(II)chelates according to the present invention may be used in conjunction with various kinds of photographic emulsions. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide, silver bromoiodide and silver chlorobromoiodide.

The hydrophilic colloid used as the vehicle for the silver halide may be, for example, gelatin, colloidal albumin, zein, casein, a cellulose derivative, a synthetic hydrophilic colloid such as polyvinyl alcohol, poly-N-vinyl pyrrolidone, etc. gelatin being however favored. If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide.

The amount of tin(II)chelate used in the processing liquids for rendering residual silver halide developable can vary within very wide limits dependent on the particular compound used and the kind of material to be processed. This amount can be determined for each particular case by simple tests. The tin(II)chelates are usually added to the processing liquid in an amount comprised between about 10 mg and about 10 g preferably between 50 mg and 2 g per liter. The choice to which processing liquid these compounds have to be added depends upon the particular type of process. Since, however, the treatment in the photographic processing liquid according to the present invention replaces an overall exposure it is obvious to carry out the treatment at that stage at which otherwise the overall exposure occurred or at an earlier stage if possible, and preferably, in the developing liquid itself, with which the light-sensitive material would be treated after the overall exposure.

A preliminary separate processing liquid containing a tin(II)chelate of a (poly)amino-(poly)carboxylic acid in acid or salt form may comprise other ingredients too such as one or more of the ingredients that otherwise would have been incorporated into the developer.

The maximum or minimum density of the images obtained can still be improved and the characteristics of the light-sensitive material can be altered by using all kinds of ingredients which are generally known in the art of emulsion preparation.

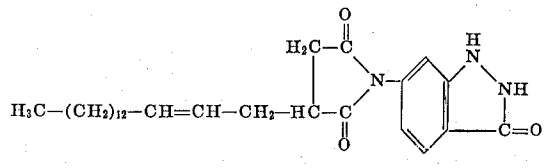
Most of these ingredients are preferably incorporated into the light-sensitive material itself, in effective contact with the silver halide emulsion layer and favorably in the latter layer itself. However, as is known many of these ingredients, may be incorporated into the developer with the same favorable result. Combinations of two or more of said ingredients, of course, may also be used.

Among the said ingredients may be mentioned some binders for at least partially replacing gelatin as a binder for the silver halide grains and referred to already above in the description, further hardening agents, stabilizers, optical sensitizers, moistening agents, etc.

The following examples illustrate the present invention.

EXAMPLE 1

A green-sensitized silver bromoiodide emulsion comprising as color coupler for magenta the compound having the following structural formula :



is coated on a conventional film support.

The material is exposed through a grey wedge and then developed for 2 ½ minute in a black-and-white developer having the following composition :

water	800 ccs
sodium hexametaphosphate	2 g
1-phenyl-3-pyrazolidone	3 g
anhydrous sodium sulphite	50 g
hydroquinone	6 g
anhydrous sodium carbonate	40 g
50 % aqueous solution of potassium thiocyanate	5 ccs
potassium bromide	2 g
water to make	1 litre

Then the material is rinsed and treated in a stop-bath having the following composition :

water	900 ccs
potassium alum	15 g
glacial acetic acid	10 ccs
borax	21 g
water to make	1,000 ccs

The element is thoroughly washed and treated for 3 minutes in the color developer with pH = 10.4 having the following composition :

N,N-diethyl-p-phenylenediamine hydrochloride	3 g
sodium hexametaphosphate	1 g
0.1 molar solution of the tin(II) chelate of compound 1	5 ccs
anhydrous sodium sulphite	4 g
anhydrous sodium carbonate	50 g
potassium bromide	0.5 g
potassium iodide	2.5 g
sodium bicarbonate	3 g
pentachloro-phenol	0.1 g
water up to	1,000 ccs

After having rinsed the material it is treated for 5 minutes in a stop bath having the following composition :

water	900 ccs
potassium alum	15 g
glacial acetic acid	10 ccs
borax	21 g
water to make	1,000 ccs

The material is once again rinsed for 5 minutes and then bleached for 7 minutes 30 seconds in the following bleach bath :

water	900 ccs
potassium hexacyanoferrate(III)	75 g
potassium bromide	15 g
glacial acetic acid	10 ccs
sodium acetate	5 g
potassium alum	15 g
water to make	1,000 ccs

The bleached material is rinsed for 2 minutes 30 seconds and then treated for 5 minutes in the following fixing solution :

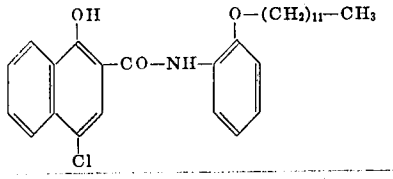
trisodium salt of ethylene diamine tetraacetic acid	1 g
anhydrous sodium thiosulphate	130 g
anhydrous sodium sulphite	10 g
anhydrous sodium carbonate	6 g
anhydrous sodium bicarbonate	14 g

Finally, the material is washed for 10 minutes.

An excellent magenta positive wedge image is obtained having a high maximum density which is at least as good as that of a positive wedge image obtained by leaving out the fogging agent in the color developer and including an overall exposure step before color development.

EXAMPLE 2

A red-sensitized silver bromo-iodide emulsion comprising as color coupler for cyan the compound having the following structural formula :



is coated on a conventional film support.

The material is exposed through a grey wedge and then processed as described in Example 1 with difference, however, that in the color developer the solution of the tin(II) chelate of compound 1 is replaced by 20 ml of a 0.1 molar solution of the tin(II) chelate of compound 10.

A cyan-positive wedge image is obtained having a high maximum density closely similar to that obtained by the conventional use of an overall exposure step before color development.

EXAMPLE 3

Example 1 is repeated with the difference however, that the chemical fogging agent is left out of the color developing bath and that before color development the material is treated in an aqueous solution comprising per liter 10 ccs of a 0.1 molar solution of the tin(II) chelate of compound 1.

An excellent magenta positive image is obtained.

EXAMPLE 4

A photographic multilayer color element comprising a support, a red-sensitized silver halide emulsion layer containing a color coupler for cyan, a green-sensitized emulsion layer containing a color coupler for a magenta, a yellow filter layer and a blue-sensitive silver halide emulsion layer containing a color coupler for yellow is image-wise exposed.

The exposed material is then developed in a black-and-white developer having the following composition :

water	800 ccs
sodium hexametaphosphate	2 g
1-phenyl-3-pyrazolidone	3 g
anhydrous sodium sulphite	50 g
hydroquinone	6 g
anhydrous sodium carbonate	40 g
50 % aqueous solution of potassium thiocyanate	5 ccs
potassium bromide	2 g
water to make	1 litre

Then the material is rinsed and treated in a stop bath having the following composition :

water	900 ccs
potassium alum	15 g
glacial acetic acid	10 ccs
borax	21 g
water to make	1,000 ccs

The element was then thoroughly washed and treated in the following color developer for 5 minutes at 25° C :

water	900 ccs
sodium hexametaphosphate	1 g
anhydrous sodium sulphite	4 g
hydroxylamine	0.3 g
N,N-diethyl-p-phenylene diamine hydrochloride	2.7 g
anhydrous sodium carbonate	25 g
0.1 molar solution of the tin(II) chelate of compound 10	2 ccs
potassium bromide	2.2 g
sodium bicarbonate	0.55 g
water to make	1 litre

After having rinsed the material for 5 minutes, it is treated for 3 minutes in the following fixing composition :

water	800 ccs
anhydrous sodium thiosulphate	200 g
sodium bisulphite	12 g
glacial acetic acid	12 ccs
borax	20 g
potassium alum	15 g
water to make	1 litre

The material is washed again for 3 min. and then treated for 3 minutes in a bleach bath having the following composition :

water	900 ccs
potassium hexacyanoferrate(III)	75 g
potassium bromide	15 g
glacial acetic acid	10 ccs
sodium acetate	5 g
potassium alum	15 g
water to make	1 litre

The material is then washed for 3 minutes and again treated for 3 minutes in the above fixing bath whereupon it is once again washed for 5 minutes.

A multicolor positive image of the original is obtained, the density of which is closely similar to that obtained when the fogging agent according to the invention is left out from the color developer and an overall exposure step is included between the black-and-white and color development step.

EXAMPLE 5

A common light-sensitive photographic black-and-white reversal silver halide film material is image-wise exposed and then processed at 20° C in the following way.

First it is developed for about 5 minutes in the following developing liquid the pH of which has been adjusted at 10.5 :

hydroquinone	2 g
monomethyl-p-amino-phenol hemisulphate	4 g
potassium bromide	2 g
sodium carbonate	40 g
sodium sulphite	40 g
potassium thiocyanate	5 g
water to make	1 litre

Then the film material is treated for about 5 minutes in the following bleach bath :

potassium dichromate	5 g
strong sulphuric acid (d = 1.85)	10 ccs
water to make	1,000 ccs

After rinsing for some minutes in water the film material is treated for 5 minutes in a clearing bath of the following composition :

sodium sulphite	100 g
water to make	1,000 ccs

After rinsing again for some minutes the film material is treated for about 6 minutes in the following developing liquid :

hydroquinone	5 g
monomethyl-p-aminophenol hemisulphate	1 g
sodium sulphite	40 g
sodium carbonate	30 g
potassium bromide	0.5 g
0.1 molar solution of the tin(II) chelate of compound 10	10 ccs
water to make	1,000 ccs

Finally the film material is rinsed and dried. A black-and-white reversal image of very good quality is obtained.

EXAMPLE 6

In order to prove the favorable fogging action of the tin(II) chelates of use according to the invention a series of tests were carried out with two identical series of photographic light-sensitive silver bromoiodide materials.

Both series I and II of materials comprise materials A having a blue-sensitive emulsion layer with color coupler for yellow, materials B having a green-sensitized emulsion layer with color coupler for magenta and materials C having a red-sensitized emulsion layer with color coupler for cyan.

The first series (I) of materials is given an overall exposure to render all silver halide developable whereupon the materials are processed as described in Example 4 from the color development step onwards, the color developer comprising however no chemical fogging agent according to the invention.

The second series (II) of materials is directly, i.e., without exposure processed as described in Example 4 from the color development step onwards, the color developer this time comprising the given chemical fogging agent of use according to the invention.

In the processed materials A, B and C yellow, magenta and cyan dyestuffs have formed respectively. The maximum densities of these dyestuffs are measured behind a blue, green and red filter respectively and are listed in the following table.

	Maximum density of dyestuff formed in—					
Series	Materials A (yellow)		Materials B (magenta)		Materials C (cyan)	
I	2.39	2.46	1.90	1.96	3.26	3.29
II	2.59	2.59	1.96	2.14	3.17	3.15

The results listed in the above table are self-explanatory and illustrate the favorable chemical fogging action of the compounds of use according to the invention as compared with an overall exposure step to light.

EXAMPLE 7

A light-sensitive photographic multilayer material which is suitable for the negative-positive processing according to the silver dye bleach process and which comprises a support, a red-sensitized silver bromide emulsion layer containing a cyan azo dye, a green-sensitized silverbromide emulsion layer containing a magenta azo dye, a yellow filter layer and a blue-sensitive silver bromide emulsion layer containing a yellow azo dye is exposed to a negative color image and processed as follows at 20° C.

The exposed material is developed for 10 minutes in a black-and-white developer having the following composition :

water	800 ccs
p-methylaminophenol sulphate	1 g
hydroquinone	3 g
anhydrous sodium sulphite	13 g
anhydrous sodium carbonate	26 g
potassium bromide	1 g
sodium hexametaphosphate	2 g
water to make	1,000 ccs

The material is rinsed for 5 minutes and treated for 5 minutes in a hardening bath of the following composition :

water	800 ccs
sodium bicarbonate	20 g
anhydrous sodium carbonate	20 g
formaldehyde (30 %)	25 ml
water to make	1,000 ccs (pH:10.8)

After having been rinsed for 5 minutes the material is treated for 5 minutes in a silver bleach bath of the following composition

water	800 ccs
potassium bichromate	10 g
concentrated sulphuric acid	25 ml
water to make	1,000 ccs (pH:1.0)

The material is rinsed for 10 minutes and developed for 10 minutes in a second black-and-white developer of the following composition :

water	800 ccs
p-methylaminophenol sulphate	1 g
hydroquinone	3 g
anhydrous sodium sulphite	13 g
anhydrous sodium carbonate	26 g
potassium bromide	1 g
solution of the tin(II)chelate of compound 1 prepared as described hereinafter	from 1 to 6 ml
water to make	1,000 ccs (pH:10.6–11)

The material, after having been rinsed for 5 minutes, is treated for 15 minutes in a silver-dye bleach bath of the following composition :

water	800 ccs
concentrated sulphuric acid	75 ccs
quinoline	50 ccs
sodium	5 g
potassium iodide	10 g
water to make	1,000 ccs (pH:0)

The material is rinsed for 5 minutes and treated for 15 minutes in a fixing solution of the following composition

water	800 ccs
anhydrous sodium sulphite	2 g
trisodium phosphate	15 g
thiosemicarbazide	2 g
ammonium thiosulphate	200 g
sodium salt of the iron(III) complex of ethylene diamine tetraacetic acid	40 g
water to make	1,000 ccs

The material is once again rinsed for 10 minutes and then dried.

No matter what amount of the tin(II)chelate solution used (from 1 to 6 ml) in the second developer, the amount of residual silver halide rendered developable was always sufficient to obtain in the silver-dye bleach bath a complete bleaching of the azo dye in the highlights. An excellent multicolor positive image is obtained.

The solution of tin(II)chelate of compound 1 added to the second developer is prepared as follows :

2.92 g of ethylene diamine tetraacetic acid and 2.8 g of sodium hydroxide are dissolved in 50 ml of water and the solution cooled below 5° C. This solution is admixed with a solution of 2.26 g of crystalline tin(II)chloride ($SnCl_2.2H_2O$) in 30 ccs of N hydrochloric acid and the mixture is stirred for 10 minutes. The solution, after having been filtered, comprises 43.95 g of the tin(II)chelate of compound 1 and its pH lies between 2 and 3.

EXAMPLE 8

In order to illustrate the favorable action of the chemical fogging agents of the invention for rendering silver halide developable a multilayer color material suitable for use in the silver dye bleach process was treated for 10 minutes, without having been exposed or subjected to a preliminary treatment, in the second black-and-white developer described in example 7 comprising 3 ml or more of the tin(II)chelate solution of compound 1. The material is then further treated as described in example 7.

A completely colorless material is obtained which proves that a sufficient amount of silver was formed to enable bleaching all of the azo dyes present.

We claim:

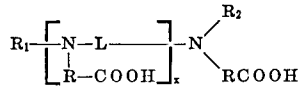
1. A method of rendering a photographic element having an image-wise distribution of silver halide developable by subjecting said element to treatment with a processing liquid comprising as a fogging agent a tin(II)chelate of a amino-carboxylic acid in acid form or in the form of a water-soluble salt

2. The method of claim 1 wherein said photographic element is simultaneously developed.

3. The method of claim 1 wherein said photographic element is subsequently developed.

4. A method of producing an image which comprises developing a photographic element comprising unexposed image-wise distributed, silver halide in the presence of a fogging agent consisting essentially of a tin(II)chelate of a (poly)amino(poly) carboxylic acid in acid form or in the form of a water-soluble salt.

5. A method according to claim 4, wherein the said (poly)amino(poly) carboxylic acid corresponds to the formula:



wherein:
L stands for alkylene,
x represents 0,1 or 2,
R stands for lower alkylene, and each of R_1 and R_2 stands for hydrogen, lower alkyl, aralkyl or aryl.

6. A method of producing an image according to claim 4, wherein said photographic element includes a reversal black-and-white material and includes the steps of first developing the exposed silver halide with a black-and-white developer; eliminating the developed silver image thus leaving an image-wise distribution of unexposed and undeveloped silver halide, and thereafter developing the residual unexposed silver halide with a black-and-white developer using said tin(II)chelate as the fogging means.

7. A method according to claim 6, wherein the developed silver image is eliminated by treatment in a photographic bleach bath.

8. A method according to claim 7 wherein said bleach bath contains potassium dichromate.

9. A method according to claim 6, wherein the said tin(II)chelate is present in said second black-and-white developer.

10. A method according to claim 9, wherein the said tin(II)chelate is present in the said second black-and-white developer in an amount comprised between 10 mg and 10 g per liter.

11. A method of producing an image according to claim 4, which comprises the steps of image-wise exposing a light-sensitive silver halide reversal color material and developing the exposed silver halide in a black-and-white developer thus leaving an image-wise distribution of un-exposed and undeveloped silver halide, developing the residual unexposed silver halide in a color developer in the presence of a color coupler and in the presence of a said tin(II)chelate, and eliminating the developed silver.

12. A method according to claim 11, wherein the developed silver is eliminated by treatment with a photographic bleach bath comprising potassium hexacyanoferrate(III).

13. A method according to claim 1, wherein the said tin(II)chelate is present in the color developer.

14. A method according to claim 11, wherein the said tin(II)chelate is present in the said color developer in an amount comprised between 10 mg and 10 g per liter.

15. A method according to claim 5, wherein said light-sensitive silver halide reversal color material is a photographic color element comprising a support bearing silver halide emulsion layers containing color couplers and which have been sensitized to different regions of the spectrum.

16. A method according to claim 15, wherein the said photographic element contains three silver halide emulsion layers, one red-sensitized and containing a cyan-forming color coupler, one green-sensitized and containing a magenta forming color coupler and one blue-sensitive containing a yellow forming color coupler.

17. A method of producing an image according to claim 4, which comprises the steps of exposing a light-sensitive silver halide color material for the silver-dye bleach process comprising a support bearing at least one silver halide emulsion layer containing an azo dye, developing the exposed silver halide in a black-and-white developer and eliminating the developed silver image thus leaving an image-wise distribution of unexposed and undeveloped silver halide, developing the remaining unexposed silver halide in a second black-and-white developer in the presence of a said tin(II)chelate, and eliminating the developed silver image formed upon said latter development as well as the azo dye in correspondence with said silver image.

18. A method according to claim 17, wherein the first developed silver image is eliminated by treatment with a silver bleach bath containing an oxidizing agent.

19. A method according to claim 18, wherein said oxidizing agent is potassium dichromate.

20. A method according to claim 17, wherein the silver image and azo dye are eliminated after the latter development by treatment with a silver-dye bleach bath.

21. A method according to claim 17, wherein the said tin(II)chelate is present in the second black-and-white developer.

22. A method according to claim 21, wherein the said tin(II)chelate is present in the second black-and-white developer in an amount comprised between 10 mg and 10 g per liter.

23. A method of producing an image according to claim 17, in which the color material for the silver dye bleach process comprises three silver halide emulsion layers, one red-sensitized and containing a cyan azo dye, one green-sensitized and containing a magenta azo dye and one blue-sensitive containing a yellow azo dye.

24. A method of producing an image according to claim 4, which comprises the steps of processing a multicolor photographic reversal element comprising a support bearing silver halide emulsion layers which have been sensitized to different regions of the spectrum, exposed and developed, to form a reversal color image in all the layers but one thus leaving in the said last layer an image-wise distribution of unexposed and undeveloped silver halide, developing the remaining layer with a color forming developer containing a color coupler in the presence of a said tin(II)chelate, and eliminating the developed silver.

25. A method according to claim 24, wherein the said tin(II)chelate is present in the last color forming developer or in a processing liquid with which the material is treated immediately prior to the said last color forming development.

26. A method according to claim 25, wherein the said tin(II)chelate is present in the said last color forming developer in an amount comprised between 10 mg and 10 g per liter.

27. The method of claim 6 wherein the said tin(II)chelate is present in a processing liquid use to treat said material after the first black-and-white development and before the second black-and-white development.

28. The method of claim 11 wherein said tin(II)chelate is present in a processing liquid with which the material is treated before the color development and after the black-and-white development.

29. The method of claim 17 wherein said tin(II)chelate is present in a processing liquid with which the material is treated after the first and before the second black-and-white development.

30. A method of producing a direct-positive image by forming in a silver halide emulsion layer of a photographic element an imagewise distribution of unexposed residual silver halide, rendering this residual silver halide developable in the presence of a chemical fogging agent consisting essentially of a tin(II) chelate of a (poly)amino(poly)carboxylic acid in acid form or in the form of a water-soluble salt and developing the residual developable silver halide.

* * * * *

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CERTIFICATE OF CORRECTION

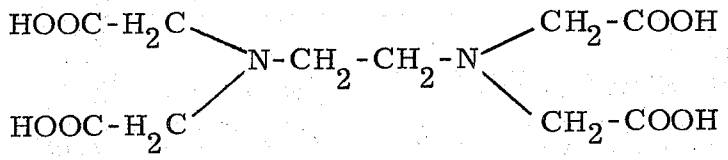
Patent No. 3,658,535 Dated April 25, 1972

Inventor(s) JOZEF FRANS WILLEMS

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

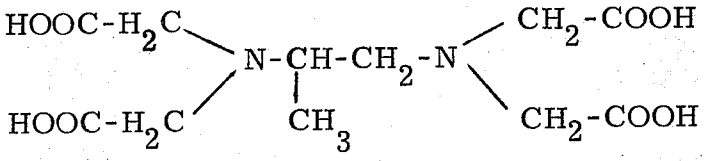
Column 2, lines 20 - 24, Formula 1, the formula should appear as follows:

1.



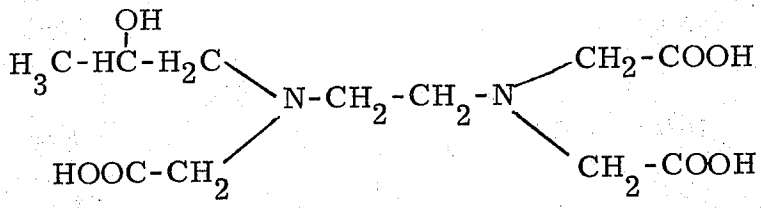
Column 2, lines 25-28, Formula 2, the formula should appear as follows:

2.



Column 2, lines 41-45, Formula 5, the formula should appear as follows:

5.



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☆ U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

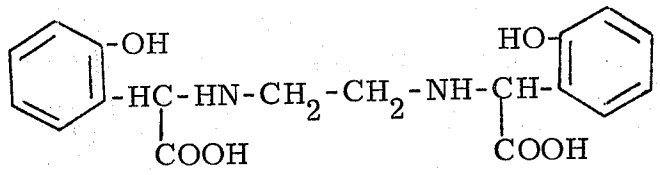
Patent No. 3,658,535 Dated April 25, 1972

Inventor(s) JOZEF FRANS WILLEMS Page 2

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

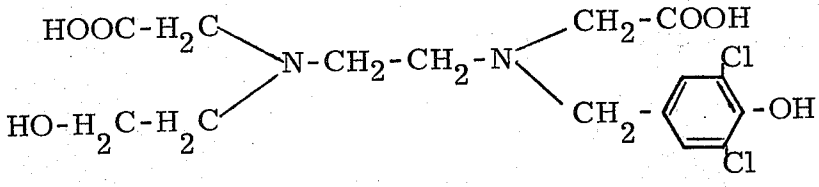
Column 2, lines 70-74, Formula 10, the formula should appear as follows:

10.



Column 3, line 48, Formula 16, "N, N'-di[3-di(2-hydroxyethyl)-amino-2-hydroxy-porpyl]-ethylenediamine," should read -- N, N'-di[3-di(2-hydroxyethyl)-amino-2-hydroxy-propyl]-ethylenediamine, --. Column 4, lines 7-11, Formula 22, the formula should appear as follows:

22.



Column 4, line 24, "comprise" should read -- comprises --. Column 11, lines 28-29, claim 1, "amino-carboxylic" should read -- (poly)amino-(poly) carboxylic --; Column 11, line 29, after "salt" insert -- . --. Column 12, line 13, claim 13, "claim 1" should read -- claim 11 --; Column 12, line 19, claim 15, "claim 5" should read -- claim 11 --. Column 13, line 10, claim 27, "use" should read -- used --.

Signed and sealed this 30th day of April 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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