United States Patent [19]

Fisch

[11] **3,773,510**

[45] **Nov. 20, 1973**

[54] **ADDITIVES TO BLEACH/FIX BATHS**

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[73] Assignee: **Minnesota Mining and Manufacturing Company**, St. Paul, Minn.

[22] Filed: **June 26, 1971**

[21] Appl. No.: **153,713**

[52] **U.S. Cl.** ..... **96/60 BF**, 96/61 R

[51] **Int. Cl.**..... **G03c 5/32**, G03c 5/38

[58] **Field of Search**..... 96/60, 60 BF, 61

[56] **References Cited**

UNITED STATES PATENTS

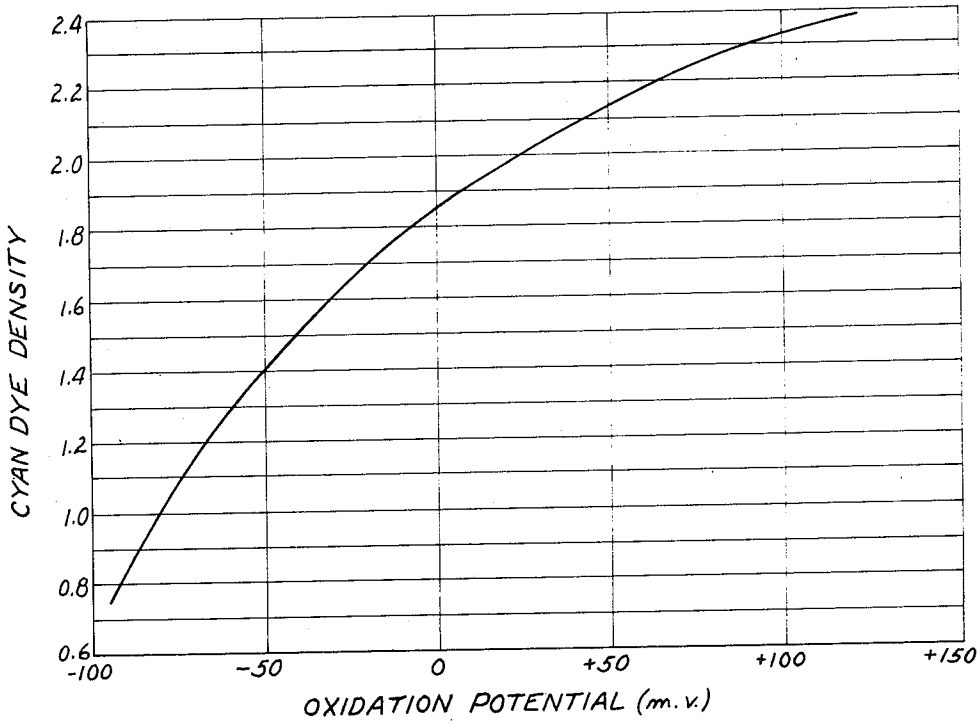
2,322,084	6/1943	Young et al.	96/53
3,335,004	8/1967	Wrisley et al.	96/22
3,619,188	11/1971	Alcock	96/60 BF

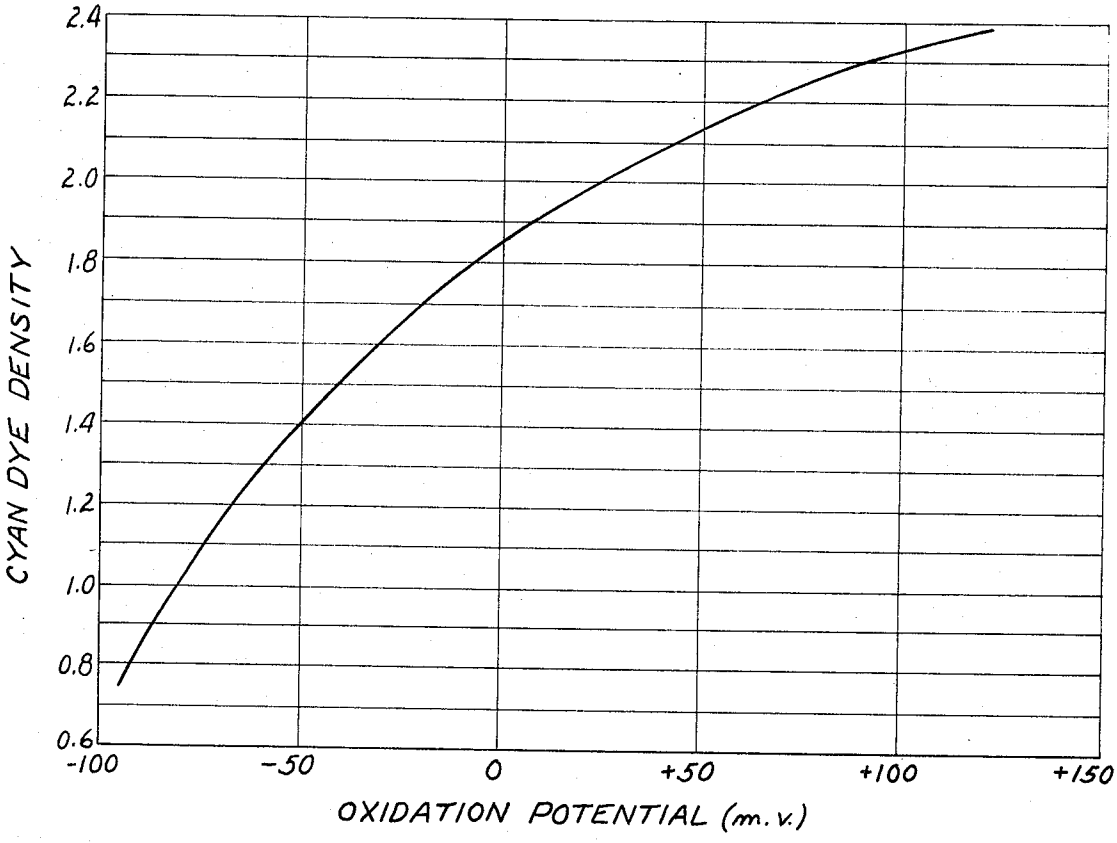
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[57] **ABSTRACT**

In a bleach/fix bath for color photographic processing, said bath having a complexed or sequestered metal oxidizing agent as the bleaching agent, the improvement which comprises a water soluble ionic compound in which one of the ionic species is inorganic and contains at least one multivalent element at one of its higher valence states, which compound increases the oxidation potential of said bath by at least 30 millivolts in a quantity not in excess of 50 grams per liter without rendering said bath unstable.

10 Claims, 1 Drawing Figure





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ADDITIVES TO BLEACH/FIX BATHS

This invention relates to color photography and more particularly to the processing of photographic material comprising silver halide emulsion layers and adapted for processing to yield color images, hereinafter referred to simply as "color photographic material."

In the conventional processing of such color photographic material, such as color print paper, a developable silver salt image is developed with an aromatic primary amino developing agent of the paraphenylene diamine type (a so-called "color developer") in the presence of a compound which will combine with the oxidation products of the color developer to form an azomethine or quinoneimine dye (a so-called "color coupler"). The dye is thus formed in situ with the developed silver image. Subsequently the product must be treated with a bleach bath and a fixing bath (or a combined bleach/fix bath) thereby to remove silver and any residual silver halide or other silver salt, leaving only the dye image. However, when a bleach/fix immediately follows the developer step there may be difficulty in effecting the full dye image. In detailing a technique to overcome such a deficiency, U.S. Pat. No. 3,189,452 describes the use of an additional oxidizing bath immediately following the bleach/fix bath to effect the formation of the full dye density available.

Great care has been taken in the past to remove unused color developer from the photographic material before the latter enters the bleach bath, usually by treatment with an acid stop bath and/or a washing operation. It is especially difficult to avoid color fogging when the stop bath is omitted, even if the pH of the bleach bath is kept below 7, except by use of a prolonged washing operation after development. Unfortunately at low pH values the cyan dyes formed by coupling of naphthol derivatives with p-phenylenediamine derivatives are converted to the colorless leuco form, so bleach/fix baths of pH values about 7 have been recommended to avoid loss of cyan dye.

We have found that the inclusion of certain additives to bleach/fix baths having a complexed or sequestered metal oxidizing agent can significantly improve the available dye density without the need for additional steps. These additives also make it possible to use pH values below 7.The additives of this invention are water soluble ionic compounds in which one of the ionic species is inorganic and contains at least one multivalent element at one of its higher valence states, which compounds increase the oxidation potential of such baths by at least 30, preferably 50, millivolts in a concentration not in excess of 50 gm/liter. The concentration used may vary greatly with the compound but obviously should not be large enough to render the bath unstable. Although the oxidation potential of the baths may be increased by lowering the pH, this technique by itself can lead to the loss of dye density (especially cyan), as mentioned earlier. The inclusion of the additives allows the formulation of bleach/fix baths with significantly increased oxidation potentials, above that of the bleach/fix alone at a given pH. This makes it possible to obtain the desired dye density without the necessity for additional processing baths or steps and further makes it possible to achieve this advantage independently of the pH of the bleach/fix bath, which is preferably above pH 4.

We have found that the preferred additives are inorganic compounds (including inorganic salts of organic acids) which contain at least one multivalent element at one of its higher valence states, including such multivalent elements as a heavy metal, oxygen, a halogen, nitrogen, sulfur, etc. Illustrative additives are the vanadates, chromates and persulfates which are soluble in and compatible with the bleach/fix baths. Examples of specific additive compounds are vanadium oxalate, cupric acetate, cupric chloride, vanadium pentoxide, potassium persulfate, sodium periodate, sodium dichromate, ceric ammonium nitrate, etc. Such bleach/fix baths contain, as the silver oxidizing agent, a complexed or sequestered metal oxidizing agent (e.g. the iron complex of ethylene diamine tetraacetic acid) and a silver solvent (usually sodium or ammonium thiosulfate, which are reducing agents).

Some of the additives encompassed by this invention have been previously used in other processes. U.S. Pat. No. 2,322,084, for example, cites the use of ammonium vanadate in a simultaneous dye and silver bleaching and fixing bath for the silver dye bleach process, which is not a conventional bleach/fix bath having a complexed or sequestered metal oxidizing agent. That process also differs from the conventional color forming process described in this invention in the fact that the "dye" essentially making up the visible image is not formed in situ but rather is present during the exposing and processing and is destroyed imagewise by the action of the silver formed by development and the bleaching bath. Some bath additives have previously been mentioned as chemical toning agents for color materials, see "History of Color Photography," J. S. Friedman (American Photography Co., Boston, 1944) pages 322 and 324. Other additives in bleach/fix baths have been used to minimize stain, accelerate fixing and accelerate bleaching. Among the reported additives are thiosemicarbizide (U.S. Pat. No. 3,293,036), thiocarbamide or ascorbic acid (British Pat. No. 777,635), sodium iodide (British Pat. No. 926,569), thiourea (British Pat. No. 991,412), mercaptotetrazole (British Pat. No. 1,138,813), and hydrazine sulfate (U.S. Pat. No. 3,293,036).

For the purpose of this invention and its examples the oxidation potential of bleach baths may be measured with a millivolt measuring device utilizing a platinum indicating electrode and a saturated calomel electrode at 20°C. As is illustrated in the examples below, dye density is seen to be directly related to the oxidation potential.

In all of the following examples a multilayer photosensitive material, specifically a color print paper containing a ketomethylene yellow coupler, a pyrazolone magenta coupler and a phenolic cyan coupler (i.e. "3M Mark III RC Color Print Paper," a product of 3M Company, Saint Paul, Minn., U.S.A.) was exposed and then processed at 85°F. in the following sequence: color developer (4 minutes), bleach/fix (4 minutes) and wash (4 minutes). A color developer containing a phenylene diamine derivative ("CD-3" color developer, a product of Eastman Kodak Company, Rochester, N.Y.) was used.

EXAMPLE 1

An aqueous bleach/fix bath was prepared using the following basic formula plus additives shown in Table I:

Sodium-ferric salt of ethylene diamine tetraacetic acid	40 grams/liter
Di-sodium salt of ethylene diamine tetraacetic acid di-hydrate	15 grams/liter
60% ammonium thiosulfate	150 grams/liter
Na_2SO_3	5 grams/liter

(pH adjusted to 4.54 with citric acid or NaOH)

Sensitometric exposures were made on a multilayer photosensitive material of the color paper type, using a step gray scale and selective colored exposure patches. The resultant dye densities were measured with a standard color densitometer.

TABLE I

Additive	Quantity of additive (grams/liter)	Oxidation Potential	Cyan Dye Density
None		− 94 m.v.	0.74
Magnesium Sulfate	5	31 94 m.v.	0.75
Sodium Nitrate	200	− 71 m.v.	0.78
Cupric Chloride	5	− 62 m.v.	1.25
Sodium Dichromate	2	− 22 m.v.	1.61
Potassium Persulfate	2	−4 m.v.	1.78
Vanadium Pentoxide	5	+110 m.v.	2.38

Using the same millivolt measuring device described above the bleach/fix formula, various other chemical compounds were incorporated into this standard solution, the resultant oxidation values were measured and recorded (the pH of each of the samples was adjusted to pH 4.5 by the use of citric acid or potassium hydroxide as needed before measuring the oxidation potential). Results are presented in Table II.

TABLE II

Sample	Additive	Quantity of additive grams/liter	Change in Oxidation Potential
Control	no additive, standard screening bath		
A	thiourea	5	0
B	magnesium sulfate	5	0
C	5 phenyl mercaptatetrazole	2	0
D	hydroxylamine sulfate	5	0
E	thiosemicarbizide	3	0
F	ethylene thiourea	5	0
G	ceric ammonium nitrate	30	+ 42
H	cupric chloride	5	+ 32
I	sodium periodate	25	+ 30
J	m-dinitrobenzene	2	0
K	sodium dichromate	2	+ 72
L	potassium persulfate	2	+ 90
M	vanadium pentoxide	5	+204
N	sodium nitrate	200	+ 25

The oxidation potentials were measured with a platinum indicating electrode and a saturated calomel electrode at 20°C. In all instances those baths which contained the additives that raised the oxidation potential at least 30 m.v. were highly effective in developing the full dye density, especially of the cyan dye. No significant increase in oxidation potential occurs when additives A - F and J were used in higher concentrations up to 50 grams/liter. The direct relationship between oxidation potential and dye density is immediately apparent from these data.

EXAMPLE 2

Sodium nitrate in amounts varying from 0 to 200 grams/liter were added to the bleach/fix formula, and the oxidation potential was measured. The following data describes the results.

TABLE III

Sodium nitrate concentration	Oxidation Potential
200 grams/liter	− 70 m.v.
125 grams/liter	− 70 m.v.
80 grams/liter	− 75 m.v.
30 grams/liter	− 82 m.v.
10 grams/liter	− 90 m.v.
0 grams/liter	− 94 m.v.

As can be seen from Table III, increasing quantities of this compound did not change the oxidation potential greatly, and the oxidation potential never increased more than 24 m.v. above that of the starting standard solution. Using the same procedures with vanadium pentoxide additive instead of sodium nitrate, the oxidation data in Table IV and the cyan dye density relationship to oxidation potential in the FIGURE, were obtained.

TABLE IV

Vanadium pentoxide concentration	Oxidation Potential
10 grams/liter	+100 m.v.
5 grams/liter	30 70 m.v.
2 grams/liter	+ 47 m.v.
0.5 grams/liter	− 37 m.v.
0 grams/liter	− 95 m.v.

A comparison of the effect of sodium nitrate and vanadium pentoxide on dye density at different concentration levels is presented in Table V.

TABLE V

Additive	Quantity of additive grams/liter	Oxidation Potential	Cyan Dye Density
(control)		− 95 m.v.	0.75
sodium nitrate	80	− 70 m.v.	0.75
sodium nitrate	200	− 70 m.v.	0.75
vanadium pentoxide	2	+ 47	2.10
vanadium pentoxide	5	+110 m.v.	2.38

With the additives of this invention the effect of increasing additive concentration on oxidation potential continues until a maximum dye density is achieved or until the solution solubility limit of the additive is reached.

What is claimed is:

1. In a bleach/fix bath for color photo-graphic processing, said bath having a pH above 4 and having a sequestered metal oxidizing agent as the bleaching agent, the improvement which comprises a water soluble ionic compound in which one of the ionic species is inorganic and contains at least one multivalent element at one of its higher valence states, which compound increases the oxidation potential of said bath by at least 30 millivolts in a quantity not in excess of 50 grams per liter without rendering said bath unstable.

2. The bleach/fix bath of claim **1** in which said multivalent element is a heavy metal.

3. The bleach/fix bath of claim **1** in which said multivalent element is chromium.

4. The bleach/fix bath of claim **1** in which said multivalent element is sulfur.

5. The bleach/fix bath of claim **1** in which said multivalent element is copper.

6. The bleach/fix bath of claim **1** in which said multivalent element is a halogen.

7. The bleach/fix bath of claim **1** in which said multivalent element is a nitrogen.

8. The bleach/fix bath of claim **1** in which said multivalent element is vanadium.

9. The bleach/fix bath of claim **1** in which said multivalent element is oxygen.

10. In a color photographic process including a development step in which an exposed silver halide image is developed with an aromatic primary amino developing agent in the presence of color coupler and a bleach-

/fix step in which a sequestered metal oxidizing agent is used as the bleaching agent, the improvement which comprises the use of a bleach fix bath having a pH above 4 and containing a water soluble ionic compound in which one of the ionic species is inorganic and contains at least one multivalent element at one of its

higher valence states, which compound increases the oxidation potential of said bath by at least 30 milli-volts in a quantity not in excess of 50 grams per liter without rendering said bath unstable.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,773,510 **Dated** November 20, 1973

Inventor(s) RICHARD S. FISCH

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

Column 3, Table I, under column headed Oxidation Potential, second item: "31 94 m.v.", should be:

-- - 94 m.v. --.

Column 4, Table IV, under column headed Oxidation Potential, second item: "30 70 m.v.", should be:

-- + 70 m.v. --.

Signed and sealed this 1st day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE 1969 O—366-334