

1

3,706,561

COMPOSITIONS FOR MAKING BLIXES

Rowland G. Mowrey and Keith H. Stephen, Rochester, and Eugene F. Wolfarth, Pittsford, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.
No Drawing. Filed Mar. 23, 1970, Ser. No. 23,022

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

U.S. Cl. 96—60 BF

14 Claims

ABSTRACT OF THE DISCLOSURE

Compositions containing a sufficient amount of (a) a water-soluble complex of a ferric ion with a pentadentate or a hexadentate primary ligand to produce, when dissolved in water, a solution containing from about 0.4 mole/liter to about 2.0 moles/liter and (b) a sufficient amount of a water-soluble monodentate secondary ligand, such as, a thiocyanate, a borate, boric acid, a fluoride or a thiourea so that the mole ratio of the thiocyanate to (a) is at least 5:1, the mole ratio of the borate, boric acid or fluoride to (a) is at least 1:1 and the mole ratio of the thiourea to (a) is at least 3:1 are advantageously used to prepare blix solutions for removing silver and silver halide in color-developed photographic processing.

This invention is related to photography, compositions for making photographic blixes, blix compositions and the use of these blix compositions for photographic processing.

In the usual processing of exposed silver-salt-sensitized multilayer multicolor-forming photographic elements, both silver and dye images are produced in the image layers by the photographic developing step or steps. The silver image and any residual silver halide in the developed photographic element are usually removed by converting the silver to a silver salt by a silver bleach solution followed by the conversion of the silver salt into a diffusible, water-soluble complex with a fixing bath and then subsequently washing the bleached and fixed photographic element to remove the silver salt complex, leaving the unobscured dye images. Blix (bleach-fix) baths are known which combine the bleaching and fixing steps into a single-process step.

The usual blix solutions for removing silver and silver halide from processed color photographic elements consist of from 20 to 60 g./l. of ferric ion complexed by a multidentate ligand and a simple silver halide solvent such as hypo in the range of from 50 to 150 g./l. The pH range is usually between pH 4.0 and 8.0. At the acid end of the pH scale, the oxidant powers of the blix are highest, but the oxidant attacks the silver halide solvent; also, the ferric ion complex is least soluble, being limited to about .25 mole/l. or about 90 g./l. At the most alkaline pH value, a blix is least reactive, is more stable, and the solubility of the complex is about .45 mole/l. or about 150 g./l. These blixes having a pH of about 8 are so slow that prohibitive time is required by these blixes to remove developed silver and residual silver halide even at the maximum concentration disclosed in the prior art.

Another important fact concerning the state of the art is that there is no practical blix for camera speed color film systems. All blixes are restricted to low silver color film systems, or reflection color print material. High silver, iodide or bromide emulsions, with high gelatin is a requirement for a camera speed color film. Often, chemical addenda, e.g., antifoggants adsorbed to silver halide grains in camera speed color films, make it difficult for the active components of blix solutions to blix silver images formed by development of these grains. Blix compositions are desired that will blix camera speed film at rates that are practical for use in processing machines.

2

Also, blixes often require complicated mixing, due to the limited solubility of the ferric ion complex. The complexes are sometimes prepared during mixing of the solution, requiring several parts to be stored for each blix solution. The making of a practical concentrate of the ferric ion complex has been impossible using the prior art.

It is, therefore, an object of our invention to provide a novel composition for preparing liquid concentrates of a ferric ion complex which may be conveniently stored and diluted if desired prior to use.

Another object of the invention is to provide a novel blix composition for removing silver from photographic elements that contain a high concentration of silver by using a ferric ion complex concentrate without dilution.

Another object is to provide a novel blix composition having a uniformly high level of blix activity as the pH of the working solution is made more alkaline.

These and still other objects of our invention are accomplished by the preparation and use of our compositions for the blix step in a color process, said composition containing:

(a) A sufficient amount of a bleaching agent for silver to produce, when dissolved in water with (b) and (c), a solution with a concentration in the range from about 0.4 mole/l. to about 2.0 moles/l. of said bleaching agent which is a salt with an unchelated cation, e.g., an alkali metal ion, ammonium ion or a water-soluble amine having an ionizable proton attached to a nitrogen atom in said amine and an anion that is a complex of a ferric ion chelated by a multidentate (i.e., pentadentate or hexadentate) primary ligand in which the complex with ferric ion is penta or hexa coordinate, and in which water occupies a hexa or hepta coordinate site, respectively, in said complex;

(b) A sufficient amount of a water-soluble monodentate secondary ligand, e.g., a thiocyanate, a borate, boric acid, a fluoride or a thiourea to produce, when dissolved in water with (a) and (c), a mole ratio of the thiocyanate to (a) of at least 5:1, a mole ratio of the borate, boric acid or of the fluoride to (a) of at least 1:1 and a mole ratio of the thiourea to (a) of at least 3:1 in order to displace the penta- or hexa-coordinate water from (a);

(c) A sufficient amount of a water-soluble silver halide fixing agent, e.g., a thiosulfate, a thiocyanate, a thiourea, a thioether, etc., to produce, when dissolved in water with (a) and (b), a concentration in the range of from 0 to about 1.5 moles/l. (in the concentrate or in solutions made by diluting the concentrate);

(d) In compositions containing a water-soluble thiosulfate, a sufficient amount of a salt of an alkali metal ion, an ammonium ion or a water-soluble organic amine with an ionizable proton attached to a nitrogen atom in the amine as the cation and an anion that is a sulfite ion or provides a source of sulfite ion, e.g., bisulfite, metabisulfite, etc.; and optionally;

(e) An uncomplexed multidentate ligand or a salt with either an alkali metal ion, an ammonium ion or a water soluble organic amine with an ionizable proton attached to a nitrogen atom in said amine as the cation and an uncomplexed polyfunctional ligand as the anion.

Our compositions are used to prepare blix compositions.

Our invention includes blix compositions in which (a) is in the concentration range from .05 mole/l. to 0.4 mole/l. when (b) is a water-soluble fluoride or borate, and (c), (d) and (e) are as already described.

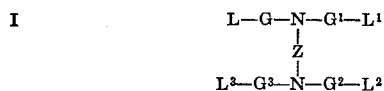
Our blix compositions are characterized by the presence of a secondary ligand which is used in sufficiently high concentration so that the water molecule is displaced from its usual position in the primary ligand-ferric ion complex. Secondary ligands used to advantage in our blix compositions include water-soluble thiocyanates,

3

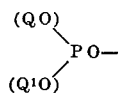
water-soluble borates, water-soluble fluorides, water-soluble thioureas, etc.

Normally, a ferric ion chelated with a pentadentate ligand has a water molecule occupying the sixth coordination site. If the complex is considered to be hexacoordinate, the water molecule occupies the heptacoordinate site. This is true in both the solid state and as a solution in water. The water will finally occupy a hexacoordinate site, displacing one of the arms of the polydentate ligand. These complexes are large organic-metallic acids and have limited solubility in the pH range of from 4-5, generally about 150 g./l. or about .45 mole/l. As the pH of such a solution is made more alkaline, the water molecule rearranges to form a bridge between two ferric ion-primary ligand molecules, thus doubling the size and weight of the complex molecule. The oxidative powers and diffusibility of this large molecule is greatly lowered. We have found that carefully selected secondary ligands used in a definite proportion, relative to primary ligand-ferric ion complex, will replace the water molecule in these complexes and thus prevent dimerization throughout the pH range of from 4 to 9.

The multidentate ligands used as primary ligands in our compositions include those having the formulas:



wherein L, L¹, L² and L³ each represent the same or different group, such as carboxy, a phosphono group (e.g.,



group, etc.); Q and Q¹ represent members such as hydrogen, an ammonium group, a water-soluble amine having an ionizable proton attached to a nitrogen atom in the amine, and represented by the formula



T, T¹ and T² each represent the same or different member, such as, hydrogen, an alkyl group, especially an alkyl group having from 1 to 6 carbon atoms (e.g., methyl, ethyl, hydroxyethyl, propyl, hydroxypropyl, methoxyethyl, chloroethyl, fluoroethyl, butyl, amyl, hexyl, cyclohexyl, etc.), an aryl group, such as, a phenyl group (e.g., phenyl, tolyl, etc.), and together R and T¹ supply the atoms required with the nitrogen atom (to which they are attached) to complete a heterocyclic ring having from 5 to 6 atoms in the ring, such as, a pyridine (e.g., pyridine, methyl pyridine, chloropyridine, etc.), a morpholine (e.g., morpholine, methyl morpholine, chloromorpholine, etc.), a piperidine (e.g., piperidine, methylpiperidine, chloropiperidine, etc.), etc. (such that not more than one of Q and Q¹ represent an ammonium group on a water-soluble amine having an ionizable proton), Q and Q¹ also represent members such as an alkyl group (e.g., methyl, ethyl, propyl, butyl, cyclopentyl, cyclohexyl, etc., including an aralkyl group, e.g., benzyl, β -phenethyl, o-acetamidobenzyl, etc., and including a heterocyclylalkyl group (e.g., pyrrolidylmethyl, pyrrolidylbutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, etc.), an aryl group, such as, a phenyl group (e.g., phenyl, tolyl, O-, p-carboxyphenyl, etc.), a naphthyl group (e.g., α -naphthyl, β -naphthyl, etc.), and a heterocyclic group (e.g., pyridyl, pyrrolyl, thiazolyl, oxazolyl, etc.); G, G¹, G² and G³ each represent the same or different divalent group, such as, a divalent hydrocarbon residue, for example: an alkylene group (e.g., an ethylene group, a propylene group, a butylene group, etc., each of which is unsubstituted or substituted with groups,

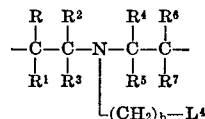
4

such as, hydroxyl, amino, nitro, halogen, a lower alkyl group, a lower alkoxy group, etc.), an arylene group (e.g., a phenylene group, a naphthylene group, etc., each of which is unsubstituted or substituted with groups such as hydroxyl, amino, nitro, halogen, a lower alkyl group, a lower alkoxy group, etc.) and a divalent heterocyclene group (e.g., a pyridylene group, a 4,5-oxazolylene group, a 4,5-thiazolylene group, etc.); and Z represents a group, such as, a

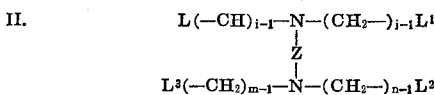


group,

a cyclohexylene group, a phenylene group, and a



group; R, R¹, R², R³, R⁴, R⁵, R⁶ and R⁷ each represent a member, such as, hydrogen, hydroxyl, an amino group, nitro, halogen, a lower alkyl group (e.g., methyl, ethyl, butyl, etc.) and a lower alkoxy group (e.g., methoxy, ethoxy, butoxy, etc.) such that no single carbon atom in the structure containing said groups R through R⁷ contains more than one hydroxyl group, more than one amino group and more than one nitro group; k represents an integer of from 2 to 4; h represents an integer of from 1 to 4 and L⁴ represents a carboxy group or a phosphono group as described previously for L, L¹, L² and L³; and



wherein L, L¹, L², L³ and Z are as defined previously for Formula I; and i, j, m and n each represent integers of from 2 to 4.

The following will illustrate typical examples of the penta and hexadentate primary ligands represented by Formulas I and II:

1. Ethylene diamine tetraacetic acid
2. Ethylene diamine tetraacetic acid di ammonium salt
3. Ethylene diamine tetraacetic acid tetra (trimethyl ammonium) salt
4. Ethylene diamine tetraacetic acid tetra (hydroxyethyl ammonium) salt
5. Pentaacetic acid diethylene triamine
6. Ethylene diamine tetraacetic acid tetra morpholinium salt
7. Ethylene diamine tetraacetic acid sodium salt
8. Ethylene diamine tetraacetic acid tetra potassium salt
9. Ethylene diamine tetraacetic acid tetra lithium salt
10. Pentaacetic acid diethylene triamine penta sodium salt
11. Pentaacetic acid diethylene triamine penta ammonium salt
12. Ethylene diamine - N-(β -hydroxyethyl)-N,N',N'-tri-acetic acid
13. Ethylene diamine - N-(β -hydroxyethyl)-N,N',N'-tri-acetic acid sodium salt
14. Ethylene diamine - N-(β -hydroxyethyl)-N,N',N'-tri-acetic acid triammonium salt
15. 1,3-diaminopropanol - N,N,N',N' - tetramethylene phosphonic acid
16. Ethylene diamine - N,N,N',N' - tetramethylene-phosphonic acid
17. 1,2 - cyclohexylenediamine-N,N,N',N'-tetramethylene-phosphonic acid
18. 1,3 - diaminopropanol - N,N,N',N'-tetramethylene-phosphonic acid
19. 1,3 - propylenediamine - N,N,N',N'-tetramethylene-phosphonic acid

5

20. 1,6 - hexylenediamine - N,N,N',N'-tetramethylene-phosphonic acid
21. Propylene diamine tetraacetic acid
22. Propylene diamine tetraacetic acid tetra sodium salt
23. Propylene diamine tetraacetic acid tetra ammonium salt
24. Propylene diamine - N - (β -hydroxyethyl)-N,N',N'-triacetic acid
25. Propylene diamine - N - (β -hydroxyethyl)-N,N',N'-triacetic acid trisodium salt
26. Propylene diamine - N - (β -hydroxyethyl)-N,N',N'-triacetic acid triammonium salt
27. (2-hydroxypropylene)diamine tetraacetic acid
28. 2-hydroxypropylene diamine tetraacetic acid tetra ammonium salt
29. 2 - hydroxypropylene diamine-N-(β -hydroxyethyl)-N,N',N'-triacetic acid
30. 2 - hydroxypropylene diamine-N-(β -hydroxyethyl)-N,N',N'-triacetic acid triammonium salt
31. Cyclohexylene diamine tetraacetic acid
32. Cyclohexylene diamine tetraacetic acid tetra ammonium salt
33. Cyclohexylene diamine-N-(β -hydroxyethyl)-N,N',N'-triacetic acid
34. Cyclohexylene diamine - N-(β -hydroxyethyl)-N,N',N'-triacetic acid trisodium salt
35. Phenylene diamine tetraacetic acid
36. Phenylene diamine - N-(β -hydroxyethyl)-N,N',N'-triacetic acid

Typical amines used to form a cation for salts used in our invention include methylamine, dimethyl amine, trimethyl amine, ethyl amine, triethyl amine, hydroxyethyl amine, di-(hydroxyethyl) amine, tri-(hydroxyethyl) amine, propyl amine, butyl amine, amyl amine, hexyl amine, cyclohexyl amine, aniline, m-toluedine, pyridine, methyl pyridine, chloropyridine, morpholine, methyl-morpholine, chloromorpholine, piperidine, etc.

Secondary ligands used to advantage according to our invention include water-soluble thiocyanates having the formula:

(III) MCNS, wherein M represents alkali metal, e.g., sodium, potassium, lithium, etc., ammonium or a water-soluble amine having an ionizable proton attached to a nitrogen atom represented by the formula:

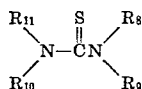


as defined and illustrated with examples previously, water-soluble borates having the formula:

(IV) M_2BO_2 , wherein M is as defined previously; (IV)(a) Boric acid; and water-soluble fluorides having the formula:

(V) MF, wherein M is as defined previously; and water-soluble thioureas having the formula:

VI.



wherein R_8 represents a member, such as, hydrogen, methyl, hydroxyethyl, etc.; R_9 represents a member, such as, hydrogen, methyl, hydroxyethyl, $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$, $-NHCH_2CH_2OH$, $-N(CH_2CH_2OH)_2$, $-N(CH_3)-CH_2CH_2OH$, etc.; R_{10} represents a member, such as, hydrogen, methyl, hydroxyethyl, $-NH_2$, $-NHCH_3$, $-N(CH_3)_2$, $-NHCH_2CH_2OH$, $-N(CH_2CH_2OH)_2$, $-N(CH_3)-CH_2CH_2OH$ etc.; and R_{11} represents a member, such as, hydrogen, methyl, hydroxyethyl, etc.; such that compounds of Formula VI contain at least one $-NH-$ group.

6

Typical secondary ligands used to advantage according to our invention include the following:

Water-soluble thiocyanates include the following:

- Sodium thiocyanate
- Potassium thiocyanate
- Lithium thiocyanate
- Ammonium thiocyanate
- Trimethylammonium thiocyanate
- Hydroxyethylammonium thiocyanate
- Morpholinium thiocyanate, etc.

Water-soluble borates include the following:

- Sodium borate
- Potassium borate
- Lithium borate
- Ammonium borate
- Hydroxyethyl ammonium borate, etc.

Water-soluble fluorides include the following:

- Sodium fluoride
- Potassium fluoride
- Lithium fluoride
- Ammonium fluoride
- Hydroxyethylammonium fluoride
- Trimethylammonium fluoride
- Morpholinium fluoride, etc., and

Water-soluble thioureas include the following:

- Thiourea
- Thiosemicarbazide
- N-methyl thiourea
- N,N-dimethyl thiosemicarbazide
- N,N-dimethyl thiourea
- N-(β -hydroxyethyl) thiourea
- N,N-di-(β -hydroxyethyl) thiourea
- Thiocarbohydrazide
- N,N,N',N'-tetramethyl thiocarbohydrazide
- N,N'-dimethylthiocarbohydrazide
- N,N'-dimethyl thiourea
- N,N'-di-(β -hydroxyethyl) thiourea
- N-(β -hydroxyethyl)-N-methylthiourea
- N'-(β -hydroxyethyl)-N-methylthiourea
- N-(β -hydroxyethyl)-N-methylthiosemicarbazide
- N,N'-di-(β -hydroxyethyl)thiocarbohydrazide

Any silver halide fixing agents are used advantageously in our compositions for component (C) on page 3 when a water-soluble fluoride, a water-soluble borate or boric acid are used as the secondary ligand or when there is not enough water-soluble thiocyanate or water-soluble thiourea to serve as both secondary ligand and silver halide solvent. Particularly advantageous silver halide solvents are those of Formulas III, VI described above, VII, i.e., $M_2S_2O_3$, where M is as defined previously and thioether compounds including those having the formula:

(VIII) $HO(CH_2CH_2Z)_pCH_2CH_2OH$

wherein p is an integer of from 2 to 13 and the Zs represent oxygen or sulfur with at least one-third of the Zs being sulfur with at least two consecutive Zs in the structure being sulfur atoms, and those having the formula:

(IV) $HOOCH_2(SCH_2CH_2)_qSCH_2COOH$

wherein q represents an integer of 1, 2 or 3 and the alkali metal, ammonium and amine salts (i.e., when the hydrogen atom of the carboxy group is replaced by M as defined previously. Representative examples of compounds of Formula VIII include 3,6-dithia-1,8-octanediol, 3,6,9-trithia-1,11-undecanediol, 3,6,9-tetrathia-1,14-tetradecanediol, etc., and representative compounds of Formula IX include ethylene-bis-thioglycolic acid, 3,6,9-trithiaheptadecanedioic acid, ethylene-bis-thioglycolic acid disodium salt, etc.

The ligands, amines and fixing agents of our compositions are well known, having been described in the chemical literature and many of these compounds are available commercially.

Our compositions are advantageously prepared and packaged as dry mixtures (with any liquid component, such as, an amine or ammonium hydroxide solution when needed in the blix advantageously packaged separately). These compositions are advantageously used for preparing either a blix concentrate for blixing photographic elements containing a high concentration of silver, or for a stock solution for subsequent dilution to make a less concentrated blix solution, or preparing a less concentrated blix solution directly from the dry components.

In one embodiment, a two-part concentrate is advantageously in which one part is a solution of (a) the complex of ferric ion with primary ligand (b) the secondary ligand and the other part is a solution of components, such as (c) fixing agent, (d) sulfite ion source, and (e) unchelated primary ligand.

Our blix concentrates containing components (a) and (b); (a), (b) and (e); or, (a), (b), (c), (d), and (e), i.e., in which (a) is used in the concentration range from about 0.4 mole/l. to about 2.0 moles/l. are used advantageously to blix photographic elements, especially the elements that contain high levels of silver, such as, above 100 mg./ft.² in each layer and levels of gelatin at or above 100 mg./ft.² which even the best prior art blix solutions are incapable of blixing. Photographic elements containing lower concentrations of silver are advantageously blixed with less concentrated blix solutions made by diluting our blix compositions to the desired concentration.

Typical bleaching and/or blixing compositions of our invention are shown above. Compositions 4, 5, 6, 7, 10, 11, 14, 15 and 21 are bleaching compositions and need from about 0.05 mole/l. to about 1.5 moles/l. of a water-soluble silver halide fixing agent to complete the blix composition. The other compositions on these pages are blixes.

and Graham, U.S. Pat. 3,046,129; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes and Godowsky, U.S. Pat. 2,252,718; Carroll et al., U.S. Pat. 2,592,243; and Schwan, U.S. Pat. 2,950,970.

Any photographic silver halide emulsions are advantageously used in elements processed with our blixing compositions. These emulsions comprise silver chloride, silver bromide, silver bromiodide, silver chlorobromide or mixtures thereof. Coarse grain or fine grain emulsions prepared by any of the well-known procedures are used. The emulsions advantageously contain any of the known chemical sensitizers, spectral sensitizers, antifoggants, stabilizers, coating aids and other addenda used in photographic elements. The silver halide emulsions advantageously contain any of the various hydrophilic colloids, such as, naturally-occurring substances, e.g., proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextrose, gum arabic, etc. and synthetic polymeric substances, such as, soluble polyvinyl compounds like poly(vinylpyrrolidone) acrylamide polymers, etc. Any of the known nondiffusible color-forming couplers known in the art are advantageously used in emulsions that contain incorporated couplers. The phenolic and naphtholic couplers are used as cyan-dye-formers; the 5-pyrazolone couplers are used as magenta-dye-formers and the open chain ketomethylene couplers are used as yellow-dye-formers. Any of the usual support materials used for photographic films and papers are advantageously used.

The photographic processes using our blix solutions use the aqueous alkaline developer solutions containing conventional developing agents, such as, hydroquinones, catechols, aminophenols, 3-pyrazolidones, phenylenediamines, ascorbic acid derivatives, etc., the primary aro-

Composition	Primary ligand ferric ion chelate	Secondary ligand	Minimum mole ratio of secondary ligand to primary ligand-ferric ion complex	Primary ligand ferric ion chelate typical concentration range
1	Ethylenedinitrilotetraacetato ferrate III hydrate Na salt.	NaSCN	5:1	150 g./l. to 300 g./l.
2	Ethylenedinitrilotetraacetato ferrate III hydrate NH ₄ salt.	NaSCN	5:1	150 g./l. to 300 g./l.
3	Ethylenedinitrilotetraacetato ferrate III hydrate Na salt.	Thiourea	3:1	150 g./l. to 200 g./l.
4	do.	Na ₂ BO ₃	1:1	20 g./l. to 200 g./l.
5	do.	NaF	1:1	20 g./l. to 200 g./l.
6	do.	(¹)	3:1	150 g./l. to 200 g./l.
7	Ethylenedinitrilotetraacetato ferrate III hydrate NH ₄ salt.	(¹)	3:1	150 g./l. to 200 g./l.
8	Ethylenedinitriolo-(β -hydroxyethyl) triacetato ferrate III hydrate.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
9	do.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
10	do.	NaF	1:1	20 g./l. to 200 g./l.
11	do.	Na ₂ BO ₃	1:1	20 g./l. to 200 g./l.
12	Propylene diamine tetraacetato ferrate III hydrate Na salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
13	Propylene diamine tetraacetato ferrate III hydrate NH ₄ salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
14	do.	(NH ₄) ₂ BO ₃	1:1	20 g./l. to 200 g./l.
15	do.	NH ₄ F	1:1	20 g./l. to 200 g./l.
16	Propylene diamine tetraacetato ferrate III hydrate Na salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
17	Propylene diamine tetraacetato ferrate III hydrate (C ₂ H ₅) ₃ NH salt.	KSCN	5:1	150 g./l. to 300 g./l.
18	Cyclohexylene diamine tetraacetato ferrate III hydrate sodium salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
19	Cyclohexylene diamine tetraacetato ferrate III hydrate NH ₄ salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
20	Cyclohexylene diamine tetraacetato ferrate III hydrate Na salt.	Thiourea	3:1	150 g./l. to 300 g./l.
21	Cyclohexylene diamine tetraacetato ferrate III hydrate NH ₄ salt.	NaF	1:1	20 g./l. to 200 g./l.
22	Diethylene triamine pentaacetato ferrate III hydrate Na salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
23	Diethylene triamine pentaacetato ferrate III hydrate NH ₄ salt.	NH ₄ SCN	5:1	150 g./l. to 300 g./l.
24	Diethylene triamine pentaacetato ferrate III hydrate Na salt.	Thiourea	3:1	150 g./l. to 200 g./l.
25	Diethylene triamine pentaacetato ferrate III hydrate NH ₄ salt.	Thiourea	3:1	150 g./l. to 200 g./l.

¹ N(β -hydroxyethyl)-N'-methylthiourea.

Our blix compositions are used advantageously in photographic processing wherever it is desired to remove silver and silver halide from an emulsion layer or layers as for example in any of the photographic elements designed for color photography, such as those containing color-forming couplers such as those described in Fröhlich et al., U.S. Pat. 2,376,679; Vittum et al., U.S. Pat. 2,322,027; Fierke et al., U.S. Pat. 2,801,171; Godowsky, U.S. Pat. 2,698,704; Barr et al., U.S. Pat. 3,227,554

matic amino developing agents being used advantageously for color development.

The following examples are included for a further understanding of our invention:

EXAMPLE 1

An aqueous Blix Concentrate X outside of our invention and disclosed in British Pat. 991,412 is made having the following composition: Sodium ethylenedinitriolo-

tetraacetato ferrate III hydrate, 150 g./l., ammonium thiocyanate 150 g./l. adjusted to a pH of 5.0 with NH_4OH or H_2SO_4 as required. A residue remains in the bottom of the container used to prepare the concentrate indicating that total solubility is not achieved. The ferric ion complex is not entirely soluble with the previously disclosed mole ratio of about 4.5:1 of secondary ligand to primary ligand. An aqueous Blix Concentrate A of our invention is prepared by dissolving, in one liter of water, the following mixture:

	G.
Sodium ethylenedinitrilotetra-acetato ferrate III hydrate	180
Ammonium thiocyanate	200

adjusted to a pH 5.0 with NH_4OH or H_2SO_4 as required. Total solution is attained. It is not obvious from Blix Concentrate X of the prior art, which is at the limit of solubility of the ferric ion complex, that increasing the concentration of a component will increase the ferric ion complex solubility. It is, however, the case; but, the secondary ligand must be at or above a mole ratio of 5:1 relative to the ferric ion complex. Blix Concentrate A, being of higher concentration than blixes of the prior art, will obviously have higher reactivity (than the prior art blixes) if used without dilution. Since thiocyanate is also a silver halide solvent, part (c) of our blix is not necessary if there is sufficient thiocyanate (usually above 150 g./l.) to give the desired silver halide solvent concentration.

EXAMPLE 2

Aqueous Blix Concentrate B of our invention is made up as in Blix Concentrate A, but to pH 6.3. Two strips of a conventional multilayer camera speed color film, containing three differently sensitized gelatino silver bromide emulsion layers containing in each layer more than 100 mg. of silver (in silver halide)/ft.² and in each layer more than 100 mg. of gelatin/ft.² and in each layer a different incorporated color-forming coupler, are light-image exposed to a wedge step tablet, then given negative development, reversal flash, color development as described by column 11, line 74 through line 36 in column 12 of Carroll et al., U.S. Pat. 2,944,900, then given an aqueous acetic acid stop bath and then one (1) strip is blixed with a prior art Blix Y and the other strip (2) is blixed with our Blix Concentrate B. The prior art Blix Y takes 10 minutes to clear the silver from strip (1) while our Blix B clears the silver from strip (2) in only 5 minutes. The prior art Blix Y used has the following composition:

Sodium ethylenedinitrilotetraacetato ferrate III hydrate	g./l. 60.0
Tetra sodium ethylenedinitrilotetraacetate	g./l. 6.7
Sodium sulfite	g./l. 12.0
Ammonium thiocyanate	g./l. 12.0
Ammonium thiosulfate (60% soln.)	ml./l. 200

pH adjusted to 6.8.

EXAMPLE 3

Blix Concentrate C of our invention is prepared by dissolving in one liter of water a mixture of:

	G.
Sodium ethylenedinitrilotetraacetato ferrate III hydrate	300
Ammonium thiocyanate	600

and the pH is adjusted to pH 6.7 by adding NH_4OH or H_2SO_4 as needed.

This is a stable liquid concentrate in which the secondary ligand is at a mole ratio of about 15:1 relative to the primary ligand. This represents a doubling of the solubility of the ferric ion complex as described in the prior art. It is stored and used either as a concentrate of our invention or with dilution.

EXAMPLE 4

Blix Concentrate D of our invention is prepared by dissolving, in one liter of water, a mixture of:

	G.
5 Ethylenedinitrilo-(β -hydroxyethyl)-triacetato ferrate III hydrate	180
Ammonium thiocyanate	200

and then adjusting the pH to 6.0, preferably by using NH_4OH or H_2SO_4 as required. At pH values above 5.0, our blix concentrates have increased activity, due not only to the greater concentration, but also due to the absence of the oxygen-bridged dimer herein described, the formation of which is prevented by the operation of our invention which uses high ratios of the secondary ligand.

In addition, this embodiment of our invention is worked at lower concentration levels of the ferric ion primary ligand complex and at lower ratios of the secondary ligands using another group of secondary ligands. For a further understanding, the following examples are included:

EXAMPLE 5

Blix Concentrate E of our invention is prepared by dissolving, in one liter of water, a mixture of:

Sodium ethylenedinitrilotetraacetato ferrate III hydrate	g. 150
Boric acid	g. 27
30 Ammonium thiosulfate (60% soln.)	ml. 166

and then adjusting the pH to 6.5, preferably by adding NH_4OH or H_2SO_4 as is required. Blix Concentrate F of our invention is prepared by dissolving, in one liter of water, a mixture of:

Sodium ethylenedinitrilotetraacetato ferrate III hydrate	g. 180
Sodium fluoride	g. 17
Sodium sulfite	g. 10
40 Ammonium thiosulfate (60% soln.)	ml. 200

and then adjusting the pH to 6.6, preferably by adding NH_4OH or H_2SO_4 as is required. Blix Concentrate Z, outside of our invention, is prepared having the following composition:

Sodium ethylenedinitrilotetraacetato ferrate III hydrate	g./l. 180
50 Oxalic acid	g./l. 63
Sodium sulfite	g./l. 10
Ammonium thiosulfate (60% soln.)	ml./l. 200

and then adjusting the pH to 7.6, preferably by adding NH_4OH or H_2SO_4 as is required. Blix Concentrates E and F of our invention, have a secondary ligand used at a mole ratio of about 1:1 with respect to the ferric ion-primary ligand complex. Dimerization is thereby suppressed and solubility is increased. Blix Concentrate Z uses a secondary ligand which increases solubility of the ferric ion complex, but decreases the blix rate as is shown by the following comparisons: Three strips of the multilayer camera speed film described in Example 2 are exposed to a wedge step tablet and processed as described in Example 2, except that Blixes E, F and Z are used in place of the blix baths used in Example 2. The blix times required to remove silver with these blixes are 6.25 mins. 7.5 mins. and 15 mins., respectively. These data clearly show the novel reactivity of our blixes and the specific nature of the secondary ligand. While the ratio of secondary ligand to ferric-ion primary ligand complex must be at least 5:1 for the thiocyanate ion, the data in this example show that ratios as low as 1:1 are advantageous for other secondary ligands, such as, boric acid and sodium fluoride, set forth in Blixes E and F, respectively, above.

11

The Blix Concentrates E and F are advantageously diluted to lower strength if the very high blix activity of the concentrates is not required as, e.g., in blixing low silver containing photographic elements, e.g., elements for reflection prints. Blix solutions using as the secondary ligands borate ion, fluoride ion, are not described in the prior art.

EXAMPLE 6

Blix Concentrate G is prepared by dissolving, in one liter of water, a mixture of:

	G
Sodium ethylenedinitrilotetraacetato ferrate III hydrate	150
Thiourea	125

and pH is adjusted to about 6.0. Blix Concentrate H is prepared like Blix Concentrate G but substituting for the 125 g. of thiourea, an equimolar amount of N(β -hydroxyethyl)-N'-methylthiourea. Blix Concentrate A of our invention, described in Example 1, and immediate Blix Concentrates G and H are each used to blix a different strip of the conventional multilayer camera speed color film described in Example 2 after light-image exposure, negative development, reversal flash, color development, acid stop bath (all as described in Example 2). Our Blix Concentrates A, G and H give results similar to that given by our Blix Concentrate B in Example 2:

Similarly, our Blix Concentrates A, B, C, D, E, F, G and H are used advantageously for blixing camera speed photographic elements at pHs other than shown specifically in the examples, but at pHs in the range of from about 5 to 9. These solutions are also advantageously used as they are, or diluted for blixing color elements which contain less silver and gelatin than the camera speed elements.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A composition comprising:

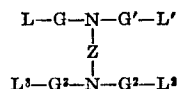
- (a) a sufficient amount of bleaching agent for silver to produce, when dissolved in water with (b) and (c), a concentration in the range of from about 0.4 mole/l. to about 2.0 moles/l. of said bleaching agent which is a salt with an unchelated cation selected from the class consisting of an alkali metal, ammonium and a water-soluble organic amine having an ionizable proton on a nitrogen atom in said amine and with an anion that is a complex of ferric ion chelated with a multidentate primary ligand;
- (b) a sufficient amount of a water-soluble monodentate secondary ligand selected from the class consisting of a thiocyanate, a fluoride and a thiourea to produce, when dissolved in water with (a) and (c), a mole ratio of said thiocyanate to (a) of at least 5:1, a mole ratio of said fluoride to (a) of at least 1:1 and a mole ratio of said thiourea to (a) of at least 3:1; and
- (c) a sufficient amount of a water-soluble silver halide fixing agent to produce, when dissolved in water with (a) and (b), a concentration in the range of from 0 to about 1.5 moles/l.

2. A blix composition comprising:

- (a) a sufficient amount of a bleaching agent for silver to produce, when dissolved in water with (b) and (c), a concentration in the range of from about 0.4 mole/l. to about 2.0 moles/l. of said bleaching agent which is a salt with an unchelated cation selected from the class consisting of an alkali metal, ammonium and a water-soluble amine having an ionizable proton on a nitrogen atom in said amine and with an anion that is a complex of ferric ion

12

chelated with a multidentate primary ligand selected from those having the formula:

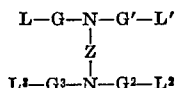


wherein L, L', L² and L³ each represent a member selected from the class consisting of a carboxy and a phosphono group; G, G', G² and G³ each represent a divalent group selected from the class consisting of an alkylene group, an arylene group and a heterocyclene group;

- (b) a sufficient amount of a water-soluble monodentate secondary ligand selected from the class consisting of a thiocyanate, a fluoride and a thiourea to produce, when dissolved in water with (a) and (c), a mole ratio of said thiocyanate to (a) of at least 5:1, a mole ratio of said fluoride to (a) of at least 1:1 and a mole ratio of said thiourea to (a) of at least 3:1; and
- (c) a sufficient amount of a water-soluble silver halide fixing agent to produce, when dissolved in water with (a) and (b), a concentration in the range of from 0 to about 1.5 moles/l., said solution being adjustable to a pH in the range of from about 5 to about 9.

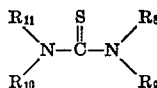
3. A blix composition comprising:

- (a) a sufficient amount of a bleaching agent for silver to produce, when dissolved in water with (b) and (c), a concentration in the range of from about 0.4 mole/l. to about 2 moles/l. of said bleaching agent which is a salt with an unchelated cation selected from the class consisting of an alkali metal, ammonium and a water-soluble amine having an ionizable proton on a nitrogen atom in said amine with an anion that is a complex of ferric ion chelated with a multidentate primary ligand selected from those having the formula:



wherein L, L', L² and L³ each represent a member selected from the class consisting of a carboxy and a phosphono group; G, G', G² and G³ each represent a divalent group selected from the class consisting of an alkylene group, an arylene group and a heterocyclene group;

- (b) a sufficient amount of a water-soluble monodentate secondary ligand selected from the class consisting of a thiocyanate, a fluoride, and a thiourea to produce, when dissolved in water with (a) and (c) a mole ratio of said thiocyanate to (a) of at least 5:1, a mole ratio of said fluoride to (a) of at least 1:1, and a mole ratio of said thiourea to (a) of at least 3:1, the said thiocyanates, borates and fluorides having a cation selected from the class consisting of an alkali metal, ammonium and a water-soluble amine having an ionizable proton on a nitrogen atom in said amine, said thiourea being selected from those having the formula:



wherein R₈ represents a member selected from the class consisting of hydrogen, methyl and hydroxyethyl; R₉ represents a member selected from the class consisting of hydrogen, methyl, hydroxyethyl, —NH₂, —NHCH₃, —N(CH₃)₂, —NHCH₂CH₂OH,



13

and $-\text{N}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{OH}$; R_{10} represents a member selected from the class consisting of hydrogen, methyl, hydroxyethyl, $-\text{NH}_2$, $-\text{NHCH}_3$,



$-\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$, and $-\text{N}(\text{CH}_3)-\text{CH}_2\text{CH}_2\text{OH}$; 5

R_{11} represents a member selected from the class consisting of hydrogen, methyl, and hydroxyethyl, said thiourea containing at least one $-\text{NH}$ -group; and

- (c) a sufficient amount of a water-soluble fixing agent selected from the class consisting of a thiosulfate, a thiocyanate, a thiourea and a thioether to produce, when dissolved in water with (a) and (b), a concentration in the range of from 0 to about 1.5 moles/l. 15

4. A composition of claim 1 in which the primary ligand is ethylenediamine tetraacetic acid.

5. A composition of claim 1 in which the primary ligand is $\text{N}-(\beta\text{-hydroxyethyl})$ ethylenediamine triacetic acid. 20

6. A blix composition of claim 1 in which the secondary ligand is ammonium thiocyanate.

7. A blix composition of claim 1 in which the secondary ligand is sodium fluoride. 25

8. A blix composition of claim 1 in which the secondary ligand is thiourea.

9. An aqueous blix composition containing 180 g./l. of sodium ethylenedinitrilotetraacetato ferrate III hydrate, 150 g./l. of ammonium thiocyanate at a pH of 5. 30

10. An aqueous blix composition containing 300 g./l. of sodium ethylenedinitrilotetraacetato ferrate III hydrate, 600 g./l. of ammonium thiocyanate at a pH of 6.7.

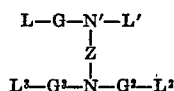
11. An aqueous blix composition containing 180 g./l. of ethylenedinitriolo (β -hydroxyethyl)triacetato ferrate III and 200 g./l. of ammonium thiocyanate at a pH of 6.0. 35

12. An aqueous blix composition containing 150 g./l. of sodium ethylenedinitrilotetraacetato ferrate III hydrate, 27 g./l. of boric acid, 166 ml./l. of 60% solution of ammonium thiosulfate at a pH of 6.5. 40

13. An aqueous blix composition containing 180 g./l. of sodium ethylenedinitrilotetraacetato ferrate III hydrate, 17 g./l. of sodium fluoride, 10 g./l. of sodium sulfite and 200 ml./l. of 60% solution of ammonium thiosulfate at a pH of 6.6. 45

14. A process for bleaching and fixing an imagewise, color-developed color element to remove silver from image areas and to remove silver halide from non-image areas, said process comprising the step of contacting said silver and said silver halide with an aqueous blix solution containing: 50

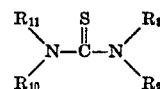
- (a) a bleaching agent in the concentration range of from about 0.4 mole/l. to about 2.0 moles/l. of said bleaching agent which is a salt with an unchelated cation selected from the class consisting of an alkali metal, ammonium and a water-soluble amine having an ionizable proton on a nitrogen atom in said amine and with an anion that is a complex of ferric ion chelated with a multidentate primary ligand selected from those having the formula: 55



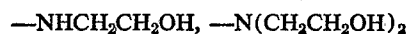
14

wherein L , L' , L^2 and L^3 each represent a member selected from the class consisting of a carboxy and a phosphono group; G , G' , G^2 and G^3 each represent a divalent group selected from the class consisting of an alkylene group, an arylene group and a heterocyclene group;

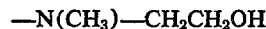
- (b) a water-soluble monodentate secondary ligand selected from the class consisting of a thiocyanate, a fluoride and a thiourea having the formula:



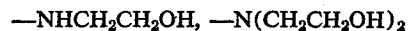
wherein R_8 represents a member selected from the class consisting of hydrogen, methyl and hydroxyethyl; R_9 represents a member selected from the class consisting of hydrogen, methyl, hydroxyethyl,



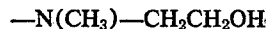
and



R_{10} represents a member selected from the class consisting of hydrogen, methyl, hydroxyethyl



and



R_{11} represents a member selected from the class consisting of hydrogen, methyl and hydroxyethyl, said thiourea containing at least one $-\text{NH}$ - group; and with a mole ratio of said thiocyanate to (a) of at least 5:1, a mole ratio of said fluoride to (a) of at least 1:1, and a mole ratio of said thiourea to (a) of at least 3:1, and

- (c) a water-soluble silver halide fixing agent in the concentration range of from 0 to about 1.5 moles/l., said blix solution containing said fixing agent when (b) is selected from the class consisting of a borate, boric acid and a fluoride until said silver and said silver halide are removed from said color-developed color element.

References Cited

UNITED STATES PATENTS

3,335,004	8/1967	Wrisley et al.	96-60
3,372,030	3/1968	Jacobson	96-60
3,578,453	5/1971	Amano et al.	96-60 BF

FOREIGN PATENTS

717,018	8/1965	Canada	96-60 BF
1,170,973	11/1969	Great Britain	96-60

60 J. TRAVIS BROWN, Primary Examiner

M. F. KELLEY, Assistant Examiner

U.S. Cl. X.R.

96-60, 61

65