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(54) Ecological cleaning liquid for photographic processor

(57) An improved ecological one-step cleaning liquid for photographic processing equipment is disclosed. The aqueous solution comprises (1) an aminopolycarboxylic acid chelate of an iron(III) salt, (2) a silver complexing agent, and (3) a silver oxidation accelerator of a particular type. Preferably, also a monophosphate salt is present.

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Description

FIELD OF THE INVENTION

[0001] The present invention deals with an improved ecological one-step cleaning liquid for photographic processing equipment.

BACKGROUND OF THE INVENTION

[0002] As it is well known conventional black-and-white photographic processing involves the consecutive use of at least three solutions being a developer which reduces the silver halide grains carrying a latent image to metallic silver, a fixing solution to remove undeveloped silver halide, and finally a wash tank to remove residual fixer. In manual tray processing a stop bath can be inserted between developer and fixer to arrest the developer, but this is usually omitted in an automatic mechanical processor by providing the fixer with a high buffering capacity.

[0003] After prolonged continuous processing unwanted deposits can form on the walls of the various processor tanks and on the mechanical roller/belt system used to transport the photographic silver halide material through the processor. These deposits are likely to soil the next sheets or stripes of processed film or paper. In the developer tank the deposits can be metallic silver, commonly referred to as "silver sludge", insoluble silver salts and alkali metal salts. In the fixer tank the deposits can be silver salts, alkali metal salts, aluminum oxides and elemental sulphur. Finally, the deposits in the wash tanks can be alkali metal salts, gelatin and gelatin by-products which induce the growth of fungi and algae.

[0004] The prior art utilizes different cleaning compositions for the various tanks. The developer tank requires a combination of a strong oxidizing agent and a silver solvent system. Commonly used prior art cleaning solutions contained chromate salts such as dichromate combined with sulphuric or sulphamic acid (see e.g. DE 1068840). Consecutively a neutralizer such as an alkali bisulfite solution was used to remove residual chromate salts. In cleaning the fixer tank a strong caustic solution is used to dissolve the salts and silver complexes. The algae and fungi slime in the wash tanks can be cleaned by a chlorine bleach such as a hypochlorite solution. From a modern ecological point of view all the chemicals cited above are agressive and hazardous to the environment. Chromium is recognized as a pollutant and a potential carcinogen. Caustic solutions are very injurious to the eyes and skin. The hypochlorite solution for cleaning the wash tank can react with residual caustic solution, used for the fixer, giving rise to the formation of toxic gaseous chlorine.

[0005] Various alternatives have been formulated in the prior art to substitute the cleaning chemicals described above.

[0006] According to US 3,625,908 the cleaning composition contains hydrogen ions, ammonium ions and sulphate ions. In the preferred embodiment it is composed of sulphuric acid, ferric ammonium sulphate and water. In CA 734388 a five-steps process is disclosed for cleaning successively all sections of an automatic processor. According to DE 2429833 an aqueous solution with a pH of at most 1.0 and containing cerium(IV) ions is used, which however is corrosive. In US 4,021,264 silver deposits are removed with an aqueous solution containing an alkali mono- or di-peroxysulphate, an alkali bisulphate and thiourea. However, the latter substance can cause photographic fog. In DE 2756010 a cleaning liquid is disclosed containing a peroxydisulphate compound, an iron(III) salt and optionally an activator. JP-A 58-048052 describes an acidic cleaning solutiuon containing iodide or bromide ions. According to US 4,678,597 the cleaning composition comprises water, a hydroxycarboxylic acid such as citric acid or tartaric acid, and a peroxymonosulphate compound. A method for cleaning photographic treating equipment with a solution containing an aminopolycarboxylic acid ferric chelate and a silver complexing agent is disclosed in JP-A 2-311845. In US 5,266,121 a two-steps cleaning metod is described using a first composition containing a chelate of an iron(III) salt plus a complexing agent, and a second composition which comprises water, an acid or acid anhydride, a surfactant and a water soluble solvent. In US 5,441,665 the aqueous cleaning composition contains a peroxocompound, preferably sodium persulphate; in most examples sulfamic acid is also present.

OBJECTS OF THE INVENTION

[0007] The present invention extends the teachings on cleaning liquids for photographic processors. It is an object of the present invention to provide an

[0008] ecologically acceptable cleaning composition for a photographic processor.

[0009] It is a further object of the present invention to provide a cleaning composition for a photographic processor with reduced cleaning time.

[0010] It is still a further object of the present invention to provide a cleaning composition which is suitable for cleaning the developer tank in just one step.

SUMMARY OF THE INVENTION

[0011] The above mentioned objects are realised by providing an aqueous cleaning composition for a photographic processor comprising,

(1) an aminopolycarboxylic acid chelate of an iron(III) salt in a concentration of at least 0.01 mole/l,
(2) a silver complexing agent in a concentration of at least 0.05 mole/l,
(3) a heterocyclic silver oxidation accelerating compound having at least two nitrogen atoms in the heterocyclic nucleus and carrying a mercapto group and not carrying a hydrophilic substituent besides said mercapto group, in a concentration of at least 0.001 mole/l.

[0012] In a preferred embodiment also a monophosphate salt, e.g. an alkali monophosphate salt, is also present in the cleaning composition.

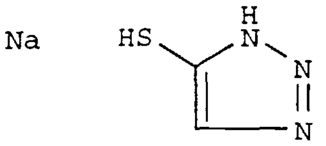
DETAILED DESCRIPTION OF THE INVENTION

[0013] A principal ingredient of the cleaning composition according to the present invention is an aminopolycarboxylic acid chelate of an iron(III) salt. This compound will take care of the oxidation of the metallic silver sludge to silver ions. Suitable chelating agents for iron(III) ions are EDTA, DTPA, hydroxy(EDTA), PDTA, MIDA, ADA and NTA. The four latter compounds show the advantage of being biodegradable. Preferred compounds are sodium iron(III) EDTA, and ammonium iron(III) EDTA. The most preferred compound is ammonium iron(III) EDTA. The concentration of the iron complex salt must be at least 0.01 mole/l in order to be effective, and is preferably comprised between 0.025 and 0.2 mole/l.

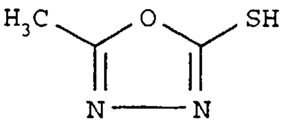
[0014] Suitable silver complexing agents include sodium-, potassium-, and ammonium thiosulphate; sodium-, potassium- or ammonium thiocyanate; sodium dithionate; alkyl alkanolamines; alkyl amines; thiourea; alkyl thiourea; cysteine HCl; ammonium dithiocarbamate. The most preferred silver complexing agent is ammonium thiosulphate. Another preferred silver complexing agent is dithiaoctanediol. The concentration of the silver complexing agent must be at least 0.05 mole/l.

[0015] An essential ingredient of the cleaning composition according to the present invention is a silver oxidizing accelerator belonging to a specific chemical class. This compound is an organic heterocyclic compound having at least two nitrogen atoms in the heterocyclic nucleus and carrying a mercapto group. Highly preferred silver oxidation accelerators according to the defined class include the compounds of following table 1 :

TABLE 1



cpd 1



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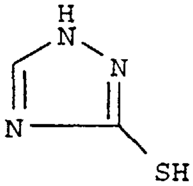

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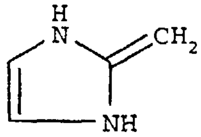

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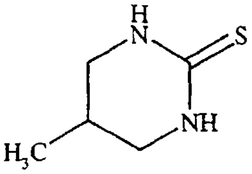

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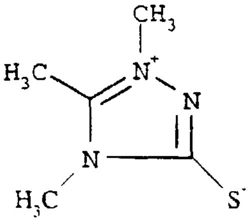

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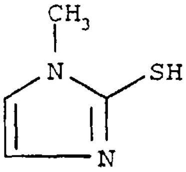

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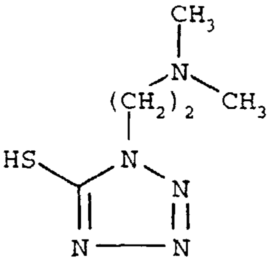
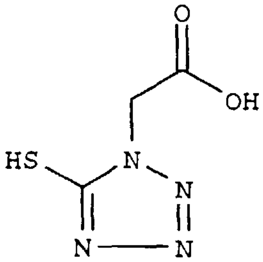


cpd 8

Na 

cpd 9

[0016] The most preferred silver oxidation accelerator is 3-mercapto-1,2,4-triazole (compound 3).

[0017] The concentration of the silver oxidation accelerator in the cleaning solution must be at least 0.001 mole/l, and is preferably comprised between 0.005 and 0.05 mole/l.

[0018] It was found experimentally that when a silver oxidation accelerator as defined above was omitted it was necessary to use high concentrations of the chelated iron(III) salt, and the presence of a monophosphate salt was indispensable. Thanks to the presence of the silver oxidation accelerator moderate concentrations of the chelated iron(III) salt can be used and the presence of a monophosphate salt becomes optional. However, in a preferred embodiment of the present invention a monophosphate salt is present preferably in a concentration between 0.02 and 0.15 mole/l. The monophosphate ion functions as a supplementary oxidation accelerator and at the same time as a buffer substance. Preferably the monophosphate salt is an alkali salt, e.g. potassium monophosphate or sodium monophosphate.

[0019] The cleaning solution can further optionally contain several other kinds of ingredients.

[0020] The composition can contain minor amounts of inorganic or organic acids, such as acetic acid and/or citric acid, in order to adjust the pH of the cleaning solution and strenghten the buffer capacity. The pH of the cleaning composition is preferably comprised between 4 and 7.

[0021] The solution can further contain a sequestering agent for complexing calcium and magnesium ions originating from hard water.

[0022] The solution can further contain sulphite ions, preferably potassium sulphite. It assures the stabilisation of the thiosulphate.

[0023] The solution can further contain one or more surfactants in order to assure good spreading activity on processor surfaces and good dispersion of silver deposits.

[0024] A practical cleaning test is performed as follows. An automatic Rapiline 66 processor (registered trademark of Agfa-Gevaert N.V.) was filled with a conventional hydroquinone/Phenidone developer and a conventional fixer. About 80 m^2 of negative working red sensitive imagesetting film was processed with 50 ml/m^2 replenishment in dark light conditions to obtain clear film and to contaminate as much as possible the developer with dissolved silver halide. After a period of sedimentation (1-3 days) the developing tank, rollers, guiding plates and walls were completely turned black and gray ("silver mirror" effect). Than the developer tank was drained. The cleaning solution was put in (ready-for-use, as concentrate, or as powder) and the processor ran for 15 minutes with the cleaning solution at 23°C. Thereafter the cleaning solution was drained and the developing tank was rinsed twice with tap water at room temperature. There is no second cleaning phase necessary. The tank was drained and the rollers, guiding plates and walls where controlled on remaining black silver deposit. The results where quoted from 0 to 5 according to an arbitrary scale. Zero means that no remaining silver deposit was found. Five means no reduction in silver deposit with regard to the start of the cleaning.

[0025] The cleaning system described is suitable for all types of photographic processors. A typical developer tank consists of the tank and the developer rack. In the tank there are sensors, heating elements, drain and replenishing pipes and circulation holes. The corners and surface around these elements are very hard to clean mechanically; only chemical cleaning is effective. The developer rack has the transport function for the immersed photographic material. This means that the possible appearance of scratches, guiding plate marks and roller marks is dependent on the quality of the rack. The entrance and the exit roller pair are the places where silver sludge contamination is most apparent, but the bottom guiding plate and rollers are the most contaminated ones. The most common places where silver sludge is transferred on the photographic material are the rollers (cause pressure and slip) and the guiding plates (cause abration due to direct contact). To prevent this heavily disturbing problem chemical cleaning of the developer is necessary as decribed here. Racks are to complex to clean mechanically. Also in closed tank and small guiding sleeves systems chemical cleaning at the spot is the only solution.

[0026] The present invention will now be illustrated by the following examples without however being limited thereto.

EXAMPLES

Example 1

[0027] This example illustrates the efficiency of the presence of several different silver oxidation accelerators and compares there activity by means of a bleach-fix test. This test is performed as follows. After 25 s of immersion in bright light in a conventional developer, and immersion in a fixer in an automatic Rapiline 66 processor of the photographic red sensitive, negative working recording paper Alliance HNp, having a silver coverage of 2.2 g/m^2, a maximum density of above 2.00 is reached. The roll material was cut in small strips of about 3x10cm. The strips where partially immersed in 250ml of different stirred cleaning solutions at room temperature. The time of immersion was 60, 50, 40, 30, 20, 10 and 0 seconds respectively. The strips where rinsed in tap water (stop function) and consequetively rinsed in fixer and tap water, and dried. The reflection density was measured with a MacBeth RD918 densitometer to follow the bleach-fixing activity and the results where put in a graph. The (interpolated) time to reach a density of 0.5 was taken as representative. A time shorter than 40 seconds is considered as good.

[0028] The actual cleaning compositions contained 0.194 mole/l ammonium Fe(III)EDTA, 0.336 mole/l ammonium thiosulphate, 0.083 mole/l potassium sulphite, 0.022 mole/l of Na-sequestrene, and 0.01 mol/l of the different silver oxidation accelerators. The pH was adjusted to 5.5 with acetic acid. The interpolated times to reach a reflection density of 0.5 are illustrated in following table 2a.

TABLE 2a

compound No.	time (s) D=0.5
cmpd 1	38
cmpd 2	29
cmpd 3	33
cmpd 4	36
cmpd 5	36
cmpd 6	38
cmpd 7	36
cmpd 8	28
cmpd 9	29
- (blank)	47

[0029] The table shows that all the tested compound are effective (time to reach D=0.5 smaller than 40 s).

[0030] Table 2b shows the bleach-fix speed of a liquid containing compound 3 compared to a blank containing no oxidation accelerator.

TABLE 2b

time (s)	Density (blank)	Density (cmpd 3)
0	2.04	2.02
10	1.89	1.71
20	1.34	1.17
30	1.05	0.55
40	0.66	0.38
50	0.43	0.39

[0031] It is clear from table 2b that the bleach-fixing is performed faster with a liquid containing compound 3.

[0032] As comparison we give hereinafter the results of the bleach-fix test (densities) performed with two prior art cleaning liquids the oxidation step of which was based on bichromate (cleaning liquid A) and on persulphate (cleaning liquid B) respectively. In both cases a second step being a complexing step was necessary.

bleachfix time	cl. liq. A	cl. liq. B
10.s	0.35	1.99
20.s	0.35	2.01
30 s	0.35	1.97
40 s	0.37	1.94

(continued)

bleachfix time	cl. liq. A	cl. liq. B
60.s	0.34	1.85
t(D=0.5)=	<10 s	>60 s
Tank cleaning:	0 (15'/23°C)	5 (arbitrary scale)

[0033] The molar compositions of cleaning liquid A and cleaning liquid B were as follows :

PHASE 1: oxidation/bleaching

[0034]

compound	conc mole/l	conc mole/l
H_2SO_4	0.108	0
sulfaminic acid	0.268	0
$K_2Cr_2O_7$	0.041	0
NaOH	0	0.100
CH_3COOH	0	0.347
Hydroquinone	0	0.036
KBr	0	0.084
ammoniumpersulphate	0	0.132

PHASE 2: Complexing phase

[0035]

compound	conc mole/l	conc mole/l
$(NH_4)_2S_2O_3$	0.925	0.701
Na_2SO_3	0.086	0
H_3BO_3	0.081	0
CH_3COONa	0.103	0
CH_3COOH	0.138	0

[0036] One sees that the bleach-fixing speed is all right for the cleaning liquid based on bichromate, which however is unecologig, but much too slow for the liquid based on persulphate. However, both comparative systems show the disadvantage of requiring a second step being a complexing phase.

Example 2

[0037] In example 2 the cleaning efficiency of cleaning solutions having different compositions are compared. The results are summarized in tables 3a and 3b.

TABLE 3a

ingredient	molar concentrations							
	C1	C2	I1	I2	I3	I4	I5	I6
Na-sequestrene	0.022	=	=	=	=	=	=	=
K_2SO_3	0.083	=	=	=	=	=	=	=
cpd 3	-	-	0.050	0.050	0.030	0.010	0.005	0.010
HAc	0.606	0.606	0.628	0.491	0.471	0.471	0.626	0.583
$(NH_4)_2S_2O_3$	0.336	0.637	0.336	=	=	=	=	=
NaH_2PO_4.2aq	0.096	=	=	=	=	=	=	0
NH_4Fe(III)EDTA	0.388	=	=	=	=	=	=	=
pH	5.11	5.11	5.11	5.50	5.50	5.50	5.11	5.50
cleaning quality	3	5	0	0	0	0	0	0.5

[0038] As already explained above the quality of the cleaning is qualitatively rated by an arbitrary scale ranging from 0 (very good) to 5 (very bad). It is clear from the table that the comparison examples (C1 and C2) containing no silver oxidation accelerator show a worse cleaning result than the invention examples (I1-I6). The example containing no sodium monophosphate gives a slightly worse result than the corresponding probe containing monophosphate.

TABLE 3b

ingredients	molar concentration					
	I6	I7	I8	I9	I10	C3
Na-sequestrene	0.022	=	=	=	=	=
K_2SO_3	0.083	=	=	=	=	=
cmpd 3	0.010	0.005	0.010	=	=	=
HAc	0.538	0.223	0.208	0.163	0.147	0.270
$(NH_4)_2S_2O_3$	0.336	=	=	=	=	=
NaH_2PO_4.2aq	0	0.032	0.096	=	=	=
NH_4Fe(III)EDTA	0.388	0.194	0.097	0.048	0.024	0.006
pH	5.50	4.45	5.50	=	=	=
cleaning quality	0.5	0.5	0	0	0	3

[0039] It is clear from table 3b that the presence and the concentration of the iron(III) complex salt is of crucial importance for the quality of the cleaning. A concentration as low as 0.006 is ineffective (comparison example C3). The examples without or with a low concentration on sodium monophosphate show again a slightly worse behaviour even at relative high concentrations of NH_4Fe(III)EDTA.

Claims

1. An aqueous cleaning composition for a photographic processor comprising,

   (1) an aminopolycarboxylic acid chelate of an iron(III) salt in a concentration of at least 0.01 mole/l,
   (2) a silver complexing agent in a concentration of at least 0.05 mole/l,
   (3) a heterocyclic silver oxidation accelerating compound having at least two nitrogen atoms in the heterocyclic nucleus and carrying a mercapto group, in a concentration of at least 0.001 mole/l.

2. An aqueous cleaning composition according to claim 1 wherein said aminopolycarboxylic acid chelate of an iron(III) salt is an EDTA chelate.

3. An aqueous cleaning composition according to claim 2 wherein said EDTA chelate is chosen from ammonium iron(III) EDTA and sodium iron(III) EDTA.

4. An aqueous cleaning composition according to any of claims 1 to 3 wherein said silver compexing agent is a thiosulphate.

5. An aqueous cleaning composition according to any of claims 1 to 4 wherein said silver oxidation accelerating compound is 3-mercapto-1,2,4-triazole.

6. An aqueous cleaning composition according to any of claims 1 to 5 wherein said composition further contains a monophosphate salt.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 2038

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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X	DE 21 02 713 A (AGFA-GEVAERT) 10 August 1972 * page 11, point 5 *	1-4	
A	DE 40 34 873 A (WOLFEN FILMFAB AG) 7 May 1992 * page 3, line 20 - line 68 *	1-5	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 October 1998	Richards, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 98 20 2038

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