(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 729 065 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.08.1996 Bulletin 1996/35

(51) Int Cl.[6]: **G03C 7/42**, D06L 3/02

(21) Application number: **96200444.6**

(22) Date of filing: **21.02.1996**

(84) Designated Contracting States:
DE FR GB

(30) Priority: **21.02.1995 US 391805**
21.02.1995 US 391993

(71) Applicant: **EASTMAN KODAK COMPANY**
Rochester, New York 14650-2201 (US)

(72) Inventors:
- **Haye, Shirleyanne Elizabeth,**
  c/o Eastman Kodak Co.
  Rochester, New York 14650-2201 (US)
- **O'Toole, Terrence Robert,**
  c/o Eastman Kodak Comp.
  Rochester, New York 14650-2201 (US)
- **Ballou, Karen Ruth,**
  c/o Eastman Kodak Company
  Rochester, New York 14650-2201 (US)

(74) Representative:
Baron, Paul Alexander Clifford et al
Kodak Limited
Patent Department
Headstone Drive
Harrow Middlesex HA1 4TY (GB)

(54) Peroxide composition and method for processing color silver halide photographic elements

(57) A simple and effective peroxide bleaching solution includes a hydrogen peroxide bleaching agent and chloride ion in an amount of at least 0.45 mol/l. An organic phosphonic acid or tertiary aminocarboxylic acid can also be present for stability. The bleaching solution is useful for bleaching developed color photographic materials containing 0 to 100 mol % silver chloride in the silver halide emulsions.

EP 0 729 065 A1

Description

The present invention relates generally to the processing of color photographic elements. More particularly, it relates to the use of hydrogen peroxide bleaching solutions comprising a certain amount of chloride ion. The compositions and the methods for their use in photography are the subject of this invention.

During processing of silver halide photographic elements, the developed silver is oxidized to a silver salt by a suitable bleaching agent. The oxidized silver is then removed from the element in a fixing step.

The most common bleaching solutions contain complexes of ferric ion and various organic ligands. One primary desire in this industry is to design bleaching compositions that are more compatible with the environment. Thus it is desirable to reduce or avoid the use of ferric complexes as bleaching agents.

Peracid bleaching solutions, such as those containing peroxide, persulfate, perborate, perphosphate, perhalogen, percarboxylic acid or percarbonate bleaching agents, offer an alternative to the ferric complex bleaching solutions. They are less expensive and present lower chemical and biological demands on the environment since their by-products can be less harmful.

While persulfate bleaching agents have low environmental impact, they have the disadvantage that their bleaching activity is slow and thus require the presence of a bleaching accelerator. The most common bleaching accelerators are thiol compounds that have offensive odors.

Because hydrogen peroxide reacts and decomposes to form water, a hydrogen peroxide based bleaching solution offers many environmental advantages over persulfate and ferric complex bleaching solutions. As a result, many publications describe hydrogen peroxide bleaching solutions, including US-A-4,277,556, US-A-4,301,236, US-A-4,454,224, US-A-4,717,649 and WO-A-92/01972.

In addition, WO-A-92/07300 and EP 0 428 101A1 describe hydrogen peroxide compositions for bleaching high chloride silver halide emulsions (that is, silver halide emulsions having more than 90 mol % silver chloride). These bleaching compositions comprise from 0.005 to 0.4 mole of chloride ions per liter of solution and have a pH in the range of 5 to 11. These particular bleaching solutions, however, fail to provide effective bleaching of silver halide emulsions having less than 90 mol % silver chloride in short bleaching times.

Despite all of the efforts of researchers in the art, no hydrogen peroxide bleaching composition has been commercialized because of various problems including vesiculation (that is, blistering of the photographic element from evolution of oxygen) and poor bleaching efficiency.

There remains a need for commercially viable hydrogen peroxide bleaching solutions that are stable and nonvesiculating. Moreover, it would be useful to have such solutions for bleaching photographic elements having silver halide emulsions containing any amount of chloride.

The noted problems are solved with a method for processing a color silver halide photographic element comprising:

bleaching an imagewise exposed and developed color silver halide photographic element containing a silver halide emulsion, with a hydrogen peroxide bleaching solution comprising:
a peroxide bleaching agent, and
chloride ions present in an amount of at least 0.45 mol/l.

This invention also provides a hydrogen peroxide bleaching solution comprising:

a hydrogen peroxide bleaching agent present in an amount of from 0.15 to 5 mol/l, and
an organic phosphonic acid or tertiary aminocarboxylic acid, or a salt thereof present in an amount of at least 0.0001 mol/l,
the solution further characterized as comprising chloride ions present in an amount of at least 0.45 mol/l.

The method of this invention provides rapid and efficient bleaching of imagewise exposed and developed color photographic elements containing silver halide emulsions, and avoids the problems noted above with known hydrogen peroxide bleaching solutions. No vesiculation was observed with the use of the present invention. Moreover, the bleaching solutions present little environmental harm.

These advantages are achieved by using a hydrogen peroxide bleaching solution that contains at least 0.45 mole of chloride ion per liter of solution. In preferred embodiments, the solution also contains an organic phosphonic acid or a tertiary aminocarboxylic acid, or a salt thereof to increase stability.

Hydrogen peroxide bleaching solutions of this invention include a conventional hydrogen peroxide bleaching agent including, but not limited to hydrogen, alkali and alkaline earth salts of peroxide, or a compound which releases or generates hydrogen peroxide in an alkaline environment. Such hydrogen peroxide precursors are well known in the art, and include for example, perborate, perphosphate, percarbonate, percarboxylate and hydrogen peroxide urea. In addition, hydrogen peroxide can be generated on site by electrolysis of aqueous solutions. Examples of peroxide

bleaching solutions are described, for example, in *Research Disclosure,* publication 36544, pages 501-541 (September, 1994). *Research Disclosure* is a publication of Kenneth Mason Publications Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ England (also available from Emsworth Design Inc., 121 West 19th Street, New York, N.Y. 10011). This reference will be referred to hereinafter as *"Research Disclosure".* Hydrogen peroxide is a preferred bleaching agent.

The amount of hydrogen peroxide (or its precursor) present in the bleaching solution is generally at least 0.15 mol/l, and from 0.15 to 5 mol/l is preferred. The optimum amount will depend upon the type of photographic element being processed. For example, for color negative films that include silver bromoiodide emulsions, more preferred amounts are from 0.9 to 3 mol/l. The most preferred amounts for silver bromoiodide emulsions are from 1.45 to 2.0 mol/l. For motion picture print films that include silver chlorobromide emulsions, a more preferred amount is from 0.15 to 1 mol/l, and the most preferred amount is from 0.35 to 0.6 mol/l. For high silver chloride elements (for example, color papers), the preferred amount is from 0.15 to 3 mol/l.

Chloride ions can be supplied to the bleaching solution as part of a simple inorganic salt, such as an ammonium or alkali metal ion salt (for example, sodium chloride, potassium chloride, lithium chloride and ammonium chloride). In addition, they can be supplied as organic complexes such as tetraalkylammonium chlorides. Preferred salts are sodium chloride and potassium chloride.

The chloride ion concentration is at least 0.35 mol/l, with from 0.45 to 2 mol/l being preferred, and from 0.45 to 1 mol/l being most preferred.

The bleaching solutions of this invention are quite simple, having only two essential components, the hydrogen peroxide bleaching agent and chloride ions. Other optional and preferred components include a buffer, and an organic phosphonic acid or a tertiary aminocarboxylic acid, both of which are defined below.

The bleaching solution of this invention is alkaline, having a pH within the general range of from 7 to 13, with a pH of from 8 to 12 being preferred, a pH of from 9 to 11 being more preferred and a pH of from 10 to 11 being most preferred. The pH can be provided by adding a conventional weak or strong base, and can be maintained by the presence of one or more suitable buffers including, but not limited to, sodium carbonate, potassium carbonate, sodium borate, potassium borate, sodium phosphate, calcium hydroxide, sodium silicate, β-alaninediacetic acid, arginine, asparagine, ethylenediamine, ethylenediaminetetraacetic acid, ethylenediaminedisuccinic acid, glycine, histidine, imidazole, isoleucine, leucine, methyliminodiacetic acid, nicotine, nitrilotriacetic acid, piperidine, proline, purine and pyrrolidine. Sodium carbonate and potassium carbonate are preferred.

The amount of useful buffer or base would be readily apparent to one skilled in the art.

The bleaching solution of this invention preferably comprises one or more organic phosphonic acids or salts thereof. Generally such compounds are represented by the structure (I) :

$$R_1N(CH_2PO_3M_2)_2$$

or (II) :

$$R_2R_3C(PO_3M_2)_2$$

wherein R_1 is hydrogen, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (such as methyl, hydroxymethyl, ethyl, isopropyl, t-butyl, hexyl, octyl, nonyl, decyl, benzyl, 4-methoxybenzyl, β-phenethyl, o-acetamidobenzyl or β-phenethyl), a substituted or unsubstituted alkylaminoalkyl group (wherein the alkyl portion of the group is as defined above, such as methylaminomethyl or ethylaminoethyl), a substituted or unsubstituted alkoxyalkyl group of 1 to 12 carbon atoms (such as methoxymethyl, methoxyethyl, propoxyethyl, phenoxymethyl, methoxymethylenemethoxymethyl or t-butoxymethyl), a substituted or unsubstituted cycloalkyl group having 5 to 10 carbon atoms forming the ring (such as cyclopentyl, cyclohexyl, cyclooctyl or 4-methylcyclohexyl), a substituted or unsubstituted aryl group having 6 to 10 carbon atoms forming the ring (such as phenyl, xylyl, tolyl, naphthyl, p-methoxyphenyl or 4-hydroxyphenyl), or a substituted or unsubstituted heterocyclic group having 5 to 10 atoms forming the ring, one or more atoms being nitrogen, oxygen or sulfur atoms besides carbon atoms [such as pyridyl, pyrimidyl, pyrrolyldimethyl, pyrrolyldibutyl, benzothiazolylmethyl, tetrahydroquinolylmethyl, 2-pyridinylmethyl, 4-(N-pyrrolidino)butyl or 2-(N-morpholino)ethyl].

R_2 is hydrogen, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (as defined above), a substituted or unsubstituted aryl group having 6 to 10 carbon atoms in the ring (as defined above), a substituted or unsubstituted cycloalkyl group having 5 to 10 carbon atoms in the ring (as defined above), a substituted or unsubstituted heterocyclic group having 5 to 10 atoms forming the ring (as defined above), $-PO_3M_2$ or $-CHR_4PO_3M_2$.

R_3 is hydrogen, hydroxyl, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (defined above) or $-PO_3M_2$.

R_4 is hydrogen, hydroxyl, a substituted or unsubstituted alkyl group of 1 to 12 carbon atoms (as defined above) or $-PO_3M_2$.

M is hydrogen or a water-soluble monovalent cation imparting water-solubility such as an alkali metal ion (for example sodium or potassium), or ammonium, pyridinium, triethanolammonium, triethylammonium ion or others readily

apparent to one skilled in the art. The two cations in each molecule do not have to be the same. Preferably, M is hydrogen, sodium or potassium.

In defining the substituted monovalent groups above (including the ring structures), useful substituents include, but are not limited to, an alkyl group, hydroxy, sulfo, carbonamido, sulfonamido, sulfamoyl, sulfonato, thialkyl, alkylcarbonamido, alkylcarbamoyl, alkylsulfonamido, alkylsulfamoyl, carboxyl, amino, halo (such as chloro or bromo) sulfono, or sulfoxo, alkoxy of 1 to 5 carbon atoms (linear or branched), $-PO_3M_2$, $-CH_2PO_3M_2$ or $-N(CH_2PO_3M_2)_2$ wherein the alkyl (linear or branched) for any of these groups has 1 to 5 carbon atoms.

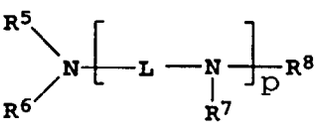
Representative phosphonic acids useful in the practice of this invention include, but are not limited to the compounds listed in EP 0 428 101A1 (page 4), as well as the following compounds:

ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid,
nitrilo-N,N,N-trimethylenephosphonic acid,
1,2-cyclohexanediamine-N,N,N',N'-tetramethylenephosphonic acid,
o-carboxyaniline-N,N-dimethylenephosphonic acid,
propylamine-N,N-dimethylenephosphonic acid,
4-(N-Pyrrolidino)butylamine-N,N-bis(methylenephosphonic acid),
1,3-diamino-2-propanol-N,N,N',N'-tetramethylenephosphonic acid,
1,3-propanediamine-N,N,N',N'-tetramethylenephosphonic acid,
1,6-hexanediamine-N,N,N',N'-tetramethylenephosphonic acid,
o-acetamidobenzylamine-N,N-dimethylenephosphonic acid,
o-toluidine-N,N-dimethylenephosphonic acid,
2-pyridylmethylamine-N,N-dimethylenephosphonic acid,
1-hydroxyethane-1,1-diphosphonic acid,
diethylenetriamine-N,N,N',N",N"-penta(methylenephosphonic acid),
1-hydroxy-2-phenylethane-1,1-diphosphonic acid,
2-hydroxyethane-1,1-diphosphonic acid,
1-hydroxyethane-1,1,2-triphosphonic acid,
2-hydroxyethane-1,1,2-triphosphonic acid,
ethane-1,1-diphosphonic acid, and
ethane-1,2-diphosphonic acid.

Most useful are 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, diethylenetriamine-N,N,N',N",N"-penta(methylenephosphonic acid), or salts thereof. The first compound is most preferred.

The amount of organic phosphonic acid used in the practice of the invention can be at least 0.0001 mol/l and generally up to 0.02 mol/l. An amount of from 0.0001 to 0.012 mol/l is preferred.

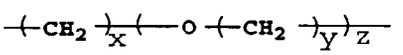
Instead of, or in addition to, the phosphonic acids (or salts thereof) described above, the bleaching solution of this invention can also contain one or more aminocarboxylic acids (or ammonium or alkali metal salts thereof) that contain a tertiary amine. These compounds can be represented by the structure (III):



wherein R^5, R^6, R^7 and R^8 are independently hydroxyalkyl of 1 to 3 carbon atoms, or carboxyalkyl of 2 to 4 carbon atoms, provided at least one of these groups is carboxyalkyl. The alkyl groups are substituted or unsubstituted and can be branched or linear. The alkyl groups can also be hydroxy-substituted. Preferably, the hydroxyalkyl or carboxyalkyl groups have methyl or ethyl groups.

In structure III, p is 0 or an integer of 1 to 3.

L is a substituted or unsubstituted alkylene group of 2 to 4 carbon atoms (linear or branched, and substituted with hydroxy or carboxy). L can also be a



group wherein x and y are independently integers of 2 to 4, and z is an integer of 1 to 3. Moreover, L can be a substituted or unsubstituted cyclic alkylene group having 6 carbon atoms in the ring (optionally substituted with hydroxy or carboxy) or a substituted or unsubstituted arylene group having 6 to 10 carbon atoms in the ring (such as phenylene or naphthylene, optionally substituted with hydroxy or carboxy). Preferably, the compound of structure III has more than one

carboxy group.

Representative tertiary aminocarboxylic acids useful in this invention include, but are not limited to, diethylenetriaminepentaacetic acid, and 2-hydroxypropylenediaminetetraacetic acid or salts thereof. The first compound is preferred.

Other addenda commonly added to hydrogen peroxide bleaching solutions can also be included, such as corrosion inhibitors, optical whitening agents, defoaming agents, calcium sequestrants, peroxide stabilizers, radical scavengers, halogen scavengers, and other materials readily apparent to one skilled in the art.

The color photographic elements to be processed using the present invention can contain any of the conventional silver halide emulsions as the photosensitive material.

In one embodiment, the emulsion contains less than 90 mole % chloride. Useful emulsions include those prepared from silver bromide, silver bromoiodide, silver chloroiodide, silver chlorobromide and silver chlorobromoiodide. The amount of silver bromide in such emulsions is preferably from 10 to 100 mole %, and the amount of silver iodide in such emulsions is from 0 to 30 mole %, and preferably less than 10 mole %.

In another embodiment, the emulsion is predominantly silver chloride. This means that at least 90 mole % of the emulsion is silver chloride. Preferably from 95 to 100 mole % is silver chloride, and most prefererably, from 99 to 100 mole % is silver chloride. The remainder of the emulsion is generally silver bromide because the emulsion contains substantially no silver iodide. This means that there is less than 1 mole % silver iodide in the emulsion.

The photographic elements processed in the practice of this invention can be single or multilayer color elements. Multilayer color elements typically contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element can be arranged in any of the various orders known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer. The elements can also contain other conventional layers such as filter layers, interlayers, subbing layers, overcoats and other layers readily apparent to one skilled in the art. A magnetic backing can be used as well as conventional supports.

Considerably more details of the element structure and components, and suitable methods of processing various types of elements are described in *Research Disclosure,* noted above. All types of emulsions can be used in the elements, including but not limited to, thin tabular grain emulsions, and either positive-working or negative-working emulsions. The elements can be either photographic films or paper elements.

The elements processed with this invention can have any desirable level of silver, but preferably, when the emulsions have 90 mole % or more of silver chloride, the elements have silver at a level of less than about 2 g/m^2, more preferably at a level of less than about 1 g/m^2 and most preferably, at a level of less than about 0.80 g/m^2 (for example from 0.4 to 0.8 g/m^2).

The elements are typically exposed to suitable radiation to form a latent image and then processed to form a visible dye image. Processing includes the step of color development in the presence of a color developing agent to reduce developable silver halide and to oxidize the color developing agent. Oxidized color developing agent in turn reacts with a color-forming coupler to yield a dye.

Color developers are well known and descrirbed in hundreds of publications including the *Research Disclosure,* noted above. In addition to color developing agents, the color developers generally contain a buffer (such as potassium carbonate), a sulfite, chelating agents, halides, and one or more antioxidants as preservatives. There are many classes of useful antioxidants including, but not limited to, hydrazines and substituted or unsubstituted hydroxylamines. By substituted hydroxylamines is meant, for example, those having one or more alkyl or aryl groups connected to the nitrogen atom. These alkyl or aryl groups can be further substituted with one or more groups such as sulfo, carboxy, hydroxy, alkoxy and other groups known in the art which provide solubilizing effects. Examples of such hydroxylamines are described, for example, in US-A-4,876,174, US-A-4,892,804, US-A-5,178,992 and US-A-5,354,646. One useful antioxidant is N-isopropyl-N-ethylsulfonic acid hydroxylamine and similar branched alkyl compounds and salts thereof.

Development can also be carried out using what is known in the art as a "developer/amplifier" solution, as described US-A-5,324,624.

Development can then followed by the use of a hydrogen peroxide bleaching solution according to the practice of this invention. The bleaching step can be carried out in any suitable fashion, as is known in the art. Color prints and films can be processed using a wide variety of processing protocols, as described for example, in *Research Disclosure,* noted above, and thus can include various combinations of one or more bleaching, fixing, washing or stabilizing steps in various orders, and lastly, drying. Additionally, reversal processes include additional steps of black and white development, chemical fogging, re-exposure, and washing prior to color development.

For the purpose of minimizing any further reaction of oxidized color developing agent with dye-bleaching, it is highly preferred that one or more additional treatments be performed between color development and bleaching as described above. Among such treatments are contacting the element with an acidic processing solution (such as dilute sulfuric or acetic acid stop bath solutions or buffer solutions, with a pH preferably of from 1 to 7); contacting the element

with a water wash bath (or rinse) having a pH ranging from 3 to 7; or wiping the photographic element with squeegee or other device that minimizes the amount of processing solution that is carried by the photographic element from one processing solution to another. Most preferably, an acidic stop bath is used between color development and peroxide bleaching.

Bleaching is generally carried out for less than 480 seconds, but longer or shorter times can be used if desired, depending upon the emulsion being processed. High chloride emulsions can have much shorter bleaching times, for example, less than 60 seconds, and preferably, less than 45 seconds. Bleaching is generally carried out at a temperature that is at or above room temperature, for example from 25 to 50 °C, and preferably from 35 to 40 °C.

Processing according to the present invention can be carried out using conventional processing equipment. Alternatively, it can be carried out using what is known in the art as "low volume thin tank" processing systems having either rack and tank or automatic tray designs. Such processing methods and equipment are described, for example, in US-A-5,436,118 and publications noted therein.

The following examples are presented to illustrate the practice of this invention, and are not intended to be limiting in any way. Unless otherwise indicated, all percentages are by weight.

Examples 1-2: Bleaching of Color Negative Films

Samples of KODAK GOLD PLUS™ 100 photographic film (containing silver bromoiodide emulsions) were exposed 1/25 second to a step wedge test object using a DLVA filter and 3000K illumination on a conventional 1B sensitometer, and processed at 38°C using the following protocol. The bleaching time was varied to determine bleaching effectiveness.

3.25 minutes	Development*
1 minute	Stop solution (1% v/v H_2SO_4)
1 minute	Water wash
0-8 minutes	Bleaching
3 minutes	Water wash
4 minutes	Fixing**
3 minutes	Water wash
1 minute	KODAK PHOTO-FLO™ rinse
5 minutes	Dry.

* The developing solution (per liter) was an aqueous solution of potassium carbonate (34.3 g), potassium hydrogen carbonate (2.3 g), sodium sulfite (3.7 g), potassium iodide (1.2 mg), sodium bromide (1.3 g), diethylenetriaminepentaacetic acid (40% w/w, 8.4 g), hydroxylamine sulfate (2.4 g) and KODAK™ Color Developing Agent CD4 (4.5 g), and had a pH of 10.05.

** The fixing solution (per liter) was an aqueous solution of sodium metabisulfite (11.8 g) and a solution (162 ml) of ammonium thiosulfate (56.5%) and ammonium sulfite (4%), and had a pH of 6.5. KODAK PHOTO-FLO™ is a commercially available rinse.

The Example 1 bleaching solution contained hydrogen peroxide (1.96 mol/l, 6% w/w), sodium chloride (0.35 mol/l) and 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l), and was adjusted to pH 10 with sodium hydroxide.

The Example 2 was similar except that it contained hydrogen peroxide at 0.98 mol/l.

Residual silver (g/m^2) was determined by X-ray fluorescence using conventional procedures. The results are tabulated below in Table I (also includes the amount of residual silver without any bleaching). Bleaching is considered complete when residual silver level is less than 0.1 g/m^2.

TABLE I

Step Number	No Bleaching (g/m^2)	Example 1: 4 minutes bleaching (g/m^2)	Example 2: 8 minutes bleaching (g/m^2)
1	1.25	0.07	0.04
2	1.19	0.06	0.06
3	1.14	0.06	0.07
4	1.10	0.07	0.06
5	1.05	0.09	0.05
6	0.99	0.08	0.04
7	0.93	0.07	0.03
8	0.87	0.06	0.04

TABLE I (continued)

Step Number	No Bleaching (g/m^2)	Example 1: 4 minutes bleaching (g/m^2)	Example 2: 8 minutes bleaching (g/m^2)
9	0.81	0.05	0.05
10	0.75	0.05	0.04
11	0.68	0.05	0.02
12	0.62	0.05	0.01
13	0.56	0.05	0
14	0.50	0.03	0
15	0.44	0.01	0
16	0.39	0.01	0.01
17	0.37	0.01	0.01
18	0.36	0.03	0.01
19	0.36	0.03	0
20	0.34	0.03	0
21	0.31	0.02	0.01

The data in Table I indicate that both bleaching solutions of this invention effectively bleached the photographic films, albeit within different times. No vesiculation was observed with these bleaching methods.

Example 3: Comparison with Known Bleaching Solution Having Low Chloride Level

This example demonstrates the use of a bleaching solution of this invention and compares its performance to that of a conventional bleaching solution (Control A). The exposure and processing protocols of Examples 1-2 were used to process samples of KODACOLOR GOLD™ 100 color film.

The Example 3 bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), sodium chloride 0.35 mol/l), sodium carbonate (0.025 mol/l), sodium bicarbonate (0.025 mol/l) and 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l). The pH was adjusted to 10 with sodium hydroxide.

The Control A solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), potassium chloride (0.067 mol/l) and potassium carbonate (0.18 mol/l). The pH was adjusted to 10 with potassium hydroxide. This peroxide bleaching solution is taught in WO-A-92/07300 (noted above).

The residual silver (g/m^2) remaining after bleaching was determined for various bleaching times using X-ray fluorescence and conventional methods. The results, evaluated at maximum density, are listed in Table II below. Bleaching was considered complete when the residual silver level was less than 0.1 g/m^2.

TABLE II

Bleaching Time (seconds)	Example 3 (g/m^2)	Control A (g/m^2)
0	1.59	1.42
60	1.06	1.28
120	0.49	0.96
240	0.17	0.51
480	0.05	0.20

It is clear from the data shown in Table II that the present invention provided faster and more complete bleaching than the peroxide bleaching solution of the prior art. No vesiculation was observed with the practice of the present invention.

Examples 4-5 Bleaching Comparisons Using Various Chloride Concentrations

Samples of KODAK GOLD PLUS 100™ color film were exposed and processed according to the protocols described above in Example 1-2. These samples were treated with three different bleaching solutions for times up to 8 minutes.

The Control C solution contained hydrogen peroxide (0.98 mol/l), sodium chloride (0.1 mol/l) and l-hydroxyethylidene-1,1-diphosphonic acid (0.012 mol/l), and its pH was adjusted to 10 using sodium hydroxide.

The Example 4 and 5 solutions were similar but contained more sodium chloride (0.35 and 0.50 mol/l, respectively).

The residual silver (g/m^2) at maximum density was measured using conventional X-ray fluorescence techniques, and the results are tabulated in Table III below. Bleaching was considered complete when the residual silver level was less than 0.1 g/m^2. Table III also contains data from conventional processing using a conventional FLEXICOLOR™ Bleach III bleaching solution (Control B).

TABLE III

Bleaching Time (sec)	Example 4	Example 5	Control B	Control C
0	1.19	1.19	1.19	1.19
60	0.50	0.56	0.10	0.54
120	0.23	0.23	0.07	0.31
240	0.12	0.09	0.06	0.17
480	0.04	0.03	0.03	0.11

These data indicate that the bleaching solutions of the present invention provide more complete bleaching than the Control C solution containing much less chloride ion. Even after 8 minutes, the Control C solution failed to bleach a significant amount of silver in the film samples. Thus, low levels of chloride ion cannot be used effectively.

Examples 6-7 Use of Various Sequestering Agents

Samples of KODAK GOLD PLUS 100™ color film were exposed and processed according to the protocols described above in Example 1-2. These samples were treated with two different bleaching solutions for times up to 8 minutes.

The Example 6 solution contained hydrogen peroxide (0.98 mol/l), sodium chloride (0.35 mol/l) and nitrilo-N,N,N-trimethylenephosphonic acid (0.004 mol/l), and its pH was adjusted to 10 using sodium hydroxide.

The Example 7 solution was similar but contained diethylenetriaminepentaacetic as the sequestering agent (0.004 mol/l).

The residual silver (g/m^2) at maximum density was measured using conventional X-ray fluorescence techniques, and the results are tabulated in Table IV below. Bleaching was considered complete when the residual silver level was less than 0.1 g/m^2. Table IV also contains data from processing without bleaching.

TABLE IV

Step No.	No Bleach	Example 6 After 8 minutes	Example 7 After 8 minutes
1	1.25	0.04	0.03
2	1.19	0.04	0.04
3	1.14	0.04	0.04
4	1.10	0.04	0.02
5	1.05	0.04	0.01
6	0.99	0.04	0.02
7	0.93	0.04	0.04
8	0.87	0.03	0.04
9	0.81	0.02	0.03
10	0.75	0.03	0.02
11	0.68	0.04	0.01
12	0.62	0.03	0.01
13	0.56	0.01	0.02
14	0.50	0.02	0.02
15	0.44	0.02	0.02
16	0.39	0.01	0.02
17	0.37	0.00	0.02
18	0.36	0.00	0.02
19	0.36	0.00	0.02
20	0.34	0.00	0.02

TABLE IV (continued)

Step No.	No Bleach	Example 6 After 8 minutes	Example 7 After 8 minutes
21	0.31	0.00	0.02

It is clear that bleaching efficiency is not impeded or improved by the use of a sequestrant. Rather, the sequestrant was added to improve solution stability.

Examples 8-11: Processing of Motion Picture Print Films

In these examples, the invention was used to process EASTMAN COLOR PRINT™ Film which contains 75 mole % chloride and 25 mole % bromide in the silver halide emulsions. Samples of this film were stepwise exposed at 1/500 second with a HA 50 and 1700 filters, and a 3000K color temperature lamp on a camera-speed sensitometer. The samples were processed at 36.7 °C using the protocol shown below. The bleaching time was varied so as to determine bleaching effectiveness.

10 seconds	Prebath*
20 seconds	Water wash
3 minutes	Development**
40 seconds	Stop solution (1% v/v H_2SO_4)
40 seconds	Water wash
0-4 minutes	Bleaching
1 minute	Water wash
40 seconds	Fixing***
1-2 minutes	Water wash
10 seconds	KODAK PHOTO-FLO™ rinse
5 minutes	Dry.

* The prebath solution (per liter) was an aqueous solution of sodium borate, decahydrate (20 g) and sodium sulfate (100 g) and had a pH of 9.25.

** The developing solution (per liter) was an aqueous solution of sodium carbonate (17.1 g), sodium sulfite (4.3 g), sodium bromide (1.7 g), aminotris (methylenephosphonic acid), pentasodium salt (40% w/w, 1 ml) and KODAK™ Color Developing Agent CD2 (2.95 g), and had a pH of 10.53.

*** The fixing solution (per liter) was an aqueous solution of sodium metabisulfite (13 g) and a solution (100 ml) of ammonium thiosulfate (56.5%) and ammonium sulfite (4%), and had a pH of 5. KODAK PHOTO-FLO™ is a commercially available rinse.

The Example 8 bleaching solution contained hydrogen peroxide (0.33 mol/l), sodium chloride (0.35 mol/l), sodium carbonate (0.025 mol/l) and sodium bicarbonate (0.025 mol/l), and its pH was adjusted to 10 using sodium hydroxide. Thus, this solution contained no phosphonic acid.

The Example 9 bleaching solution contained hydrogen peroxide (0.33 mol/l), sodium chloride (0.35 mol/l), sodium carbonate (0.025 mol/l), sodium bicarbonate (0.025 mol/l) and 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l), and its pH was adjusted to 10 using sodium hydroxide.

The Control D solution was prepared as described in EP-A-0 428 101A1, and contained potassium carbonate (21 g/l), potassium bicarbonate (6 g/l), hydrogen peroxide (0.5 mol/l), sodium chloride (0.035 mol/l), and 1-hydroxyethylidene-1,1-diphosphonic acid (8 g/l), and was adjusted to pH 10 using sodium hydroxide.

Residual silver (g/m^2) was determined at maximum density by X-ray fluorescence. The resulting data are provided in Table V below. Bleaching was considered complete when the residual silver level was less than 0.05 g/m^2.

TABLE V

Bleaching Time (seconds)	Example 8 (g/m^2)	Example 9 (g/m^2)	Control D (g/m^2)
0	1.49	1.71	1.6
15	0.18	0.04	0.63
30	0.03	0.02	0.34
60	0.02	0.01	0.01

The data in Table V show that the two peroxide solutions of this invention (with and without phosphonic acid) effectively and rapidly (within 30 seconds) bleached the noted photographic elements.

In Examples 10 and 11, similar peroxide bleaching solutions (but with peroxide concentrations of 0.15 mol/l, and 0.57 mol/l, respectively) were effectively used to bleach samples of the same film within 30-60 seconds using the same

processing protocol.

It was observed that the Control D solution (containing a lower level of chloride ion than described for this invention) was a slower bleaching solution and produced vesiculation in the film.

It was also observed that the alkaline bleaching solution of the present invention cannot be used in the conventional EASTMAN COLOR PRINT™ Film process because the first fixing solution (prior to bleaching) poisons the developed silver, causing poor bleaching efficiency by these peroxide bleaches. However, the present invention may be useful in the processing of color print films where the sound tracks are digitally or magnetically recorded since a fixing step is not required prior to bleaching.

Example 12: Bleaching Of Photographic Paper Containing Chloride Emulsion

Samples of EKTACOLOR EDGE™ Color Paper (containing more than 90 mole % chloride emulsions) were exposed 1/10 second to a step wedge test object using HA-50 and NP-11 filers, a 0.3 Inconel and 3000K illumination on a conventional 1B sensitometer, and processed using the following protocol (all steps under nitrogen). The bleaching time was varied to determine bleaching effectiveness.

45 seconds	35 °C	Development*
30 seconds	35 °C	Stop solution (1% v/v H_2SO_4)
30 seconds	33.3 °C	Water wash
0-2 minutes	35 °C	Bleaching
30 seconds	33.3 °C	Water wash
1 minutes	35 °C	Fixing**
2 minutes	33.3 °C	Water wash

* The developing solution (per liter) was the conventional KODAK EKTACOLOR™ RA Color Developer.

** The fixing solution (per liter) was an aqueous solution of sodium metabisulfite (11.8 g) and a solution (162 ml) of ammonium thiosulfate (56.5%) and ammonium sulfite (4%), and had a pH of 6.5.

The example 12 bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), sodium chloride (0.35 mol/l), potassium carbonate (0.036 mol/l) and potassium bicarbonate (0.064 mol/l), and was adjusted to pH 10 with sodium hydroxide.

A Control E bleaching solution was a conventional KODAK EKTACOLOR™ RA bleach-fixing solution containing (per liter) ferric ethylenedinitrilotetraacetate bleaching agent (50 g), ammonium thiosulfate (58%, 80 ml), sodium sulfite (7.5 g), glacial acetic acid (5 ml) and silver (3 g), and having a pH of 6.2.

A Control F bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w) only and was adjusted to pH 10 with potassium hydroxide.

A Control G bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), potassium carbonate (0.036 mol/l) and potassium bicarbonate (0.064 mol/l) and was adjusted to pH 10 with potassium hydroxide.

Residual silver (g/m^2) at maximum density was determined by X-ray fluorescence using conventional procedures. The results are tabulated below in Table VI. Bleaching was considered complete when the residual silver level was less than 0.05 g/m^2.

TABLE VI

Bleaching Time (seconds)	Example 12 (g/m^2)	Control E (g/m^2)	Control F (g/m^2)	Control G (g/m^2)
0	0.73	0.72	0.75	0.73
15	0.01	0.07	0.60	0.62
30	0	0.04	0.69	0.67
60	0	0.04	0.65	0.69

TABLE VI (continued)

Bleaching Time (seconds)	Example 12 (g/m^2)	Control E (g/m^2)	Control F (g/m^2)	Control G (g/m^2)
120	0	0.04	0.69	0.67

The data in Table VI show that practice of the present invention rapidly and effectively bleached the photographic element, and was comparable to the conventional bleaching (Control E). The Control F and G solutions failed to satisfactorily bleach the element even after two minutes of bleaching time. No vesiculation was observed with the practice of this invention.

Examples 13-14: Processing Of Color Paper With & Without Phosphonic Acid

Two bleaching solutions were compared to a bleaching solution taught in WO-A-92/07300 (noted above), identified herein as Control H, in processing samples of EKTACOLOR EDGE™ Color Paper. The samples were exposed and processed using the protocol described in Example 12.

The Example 13 bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), potassium chloride (0.5 mol/l), 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l), potassium carbonate (0.058 mol/l) and potassium bicarbonate (0.122 mol/l), and was adjusted to pH 10 with potassium hydroxide.

The Example 14 bleaching solution was similar to Example 13 bleaching solution except that the diphosphonic acid was omitted.

The Control H bleaching solution contained hydrogen peroxide (0.98 mol/l, 3% w/w), potassium chloride (0.067 mol/l) and potassium carbonate (0.18 mol/l), and was adjusted to pH 10 with potassium hydroxide.

Residual silver (g/m^2) was measured after 45 seconds of bleaching by X-ray fluorescence using conventional procedures. The resulting data at several exposure levels are tabulated in Table VII below. Bleaching was considered complete when the residual silver level was less than 0.05 g/m^2.

TABLE VII

Exposure Step Number	Example 13 (g/m^2)	Example 14 (g/m^2)	Control H (g/m^2)
1	0.02	0.01	0.02
3	0.03	0.01	0.01
5	0.01	0.01	0.01
7	0.01	0	0.03
9	0.01	0.01	0.01
11	0	0	0.02
13	0	0	0.01
15	0.01	0	0.01
17	0	0	0
19	0.01	0	0.02
21	0	0	0.01

The data in Table VII show all three bleaching solutions were effective to bleach the elements within 45 seconds. However, vesiculation was observed using the Control H prior art solution. No vesiculation was observed when the present invention was practiced.

Example 15: Processing with Low Amounts of Peroxide

The present invention was used to process samples of EKTACOLOR EDGE™ Color Paper as described above in Example 12, except that the amount of hydrogen peroxide bleaching agent was lowered to 0.49 mol/l.

The Example 15 bleaching solution contained hydrogen peroxide (0.49 mol/l, 1.5% w/w), sodium chloride (0.5 mol/l), 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l), potassium carbonate (0.025 mol/l) and potassium bicarbonate (0.025 mol/l), and was adjusted to pH 10 with sodium hydroxide.

A Control I bleaching solution was prepared as taught in EP 0 428 101A1, containing hydrogen peroxide (0.49 mol/l, 1.5% w/w), sodium chloride (0.035 mol/l), 1-hydroxyethylidene-1,1-diphosphonic acid (0.005 mol/l), potassium carbonate (0.015 mol/l) and potassium bicarbonate (0.06 mol/l), and was adjusted to pH 10 with sodium hydroxide.

Residual silver was measured after 45 seconds using X-ray fluorescence and conventional procedures. The results are tabulated below in Table VIII for various exposure densities. Bleaching was considered complete when the residual

silver level was less than 0.05 g/m^2.

TABLE VIII

Step Number	Example 15 (g/m^2)	Control I (g/m^2)
1	0.02	0.02
3	0	0
5	0.02	0.02
7	0.03	0.03
9	0.01	0.02
11	0.02	0.03
13	0	0
15	0	0
17	0.03	0.01
19	0.01	0.01
21	0	0

These data show that both bleaching solutions were effective within 45 seconds bleaching time. However, vesiculation was observed with the Control I solution. None was observed with the present invention.

Example 16: Processing of Color Negative Films Using Higher Chloride Ion Levels

The present invention was used to process samples of KODAK EKTACOLOR EDGE™ Color Paper which were exposed and processed using the protocol described in Example 12.

The Example 16 bleaching solution contained hydrogen peroxide (0.98 mol/l, 3%), sodium chloride (0.5 mol/l) and potassium carbonate buffer (0.05 mol/l), and was adjusted to pH 10 with sodium hydroxide.

In addition, different samples of the same photographic element were similarly processed using the Control E bleaching solution described above.

Residual silver (g/m^2) at maximum density was determined by X-ray fluorescence using conventional procedures. The results are tabulated below in Table IX. Bleaching was considered complete when the residual silver level was less than 0.05 g/m^2.

TABLE IX

Bleaching Time (sec)	Example 12 (g/m^2)	Control E (g/m^2)
0	0.75	0.75
15	0.02	0.07
30	0.02	0.04
45	0.01	0.04
60	0.01	0.03
120	0.00	0.02

These data clearly show that the use of the present invention, wherein the hydrogen peroxide bleaching solution contains at least 0.45 mole of chloride ion per liter of solution, rapidly (less than 15 seconds) and effectively bleached the photographic paper (less than 0.02 g Ag/m^2). The Control E solution, a conventional ferric complex bleach-fixing solution was not quite as rapid or effective.

The method described in this example should also be compared to the use of chloride ion at only 0.4 mol/l as described in EP-A-0 428 101A (page 51, runs 8 and 9). In "Run 8", the hydrogen peroxide bleaching of the high silver chloride paper after 15 seconds left 0.04 g residual silver per m^2. This is more than twice the amount of residual silver remaining after use of the present invention. In other words, at the rapid bleaching time of 15 seconds, the present invention (using > 0.45 g Cl^-/l) was more effective than the process described in the reference (using 0.4 g Cl^-/l).

It can also be seen from "Run 9" in the reference that 50 seconds bleaching time was required to reduce the residual silver to 0.01 g/m. However, if the bleaching time is increased, the Dmin values were undesirably increased. Hence, the reference teaches decreased bleaching time, but in following this teaching, bleaching is incomplete. The present invention has solved that problem by increasing chloride ion level beyond that suggested in the reference.

Example 17: Processing of Motion Picture Films Using Higher Chloride Ion Levels

The processing method described above in Examples 8 - 11 was used to process imagewise exposed samples of EASTMAN COLOR PRINT™ Film. The bleaching solution contained sodium chloride (see Table X below), hydrogen peroxide (see Table X), sodium carbonate (0.05 mol/l) and 1-hydroxyethylidene-1,1-diphosphonic acid (0.004 mol/l).

Residual silver (g/m^2) was determined at maximum density by conventional X-ray fluoresence techniques after two different bleaching times (30 and 60 seconds). The initial silver coverage was 1.58 g/m^2. The data obtained from processing are listed in Table X below. Bleaching was considered complete when the residual silver level was less than 0.05 g/m^2.

TABLE X

Film Sample	Chloride (ml/l)	Peroxide (mol/l)	pH	Residual Silver (g/m^2)	
				30 sec.	60 sec.
1	0.50	0.33	10.0	0.09	0.02
2	0.50	0.50	10.0	0.01	0.00
3	0.50	0.33	10.3	0.03	0.02
4	0.50	0.50	10.3	0.02	0.01
5	1.0	0.33	10.0	0.19	0.05
6	1.0	1.0	10.0	0.01	0.01
7	1.0	0.33	10.5	0.03	0.02
8*	1.0	1.0	10.5	0.01	0.01

* Slight vesiculation observed

Comparing the results of Example 9 (above) and the results from samples 1 and 5 of this example, it is seen that increasing the level of chloride ion in the bleaching solution slightly decreases the bleaching rate, but this effect can be overcome by increasing either the amount of peroxide or the pH (for example samples 2 and 6 for increased peroxide, and samples 3 and 7 for increased pH).

Claims

1. A hydrogen peroxide bleaching solution comprising:

a hydrogen peroxide bleaching agent present in an amount of from 0.15 to 5 mol/l, and
an organic phosphonic acid, a tertiary aminocarboxylic acid, or salt thereof present in an amount of at least 0.0001 mol/l,
the solution characterized as further comprising chloride ions present in an amount of at least 0.45 mol/l.

2. The solution as claimed in claim 1 wherein the chloride ions are present in an amount of from 0.45 to 2 mol/l,

the organic phosphonic acid or salt thereof has the structure (I) :

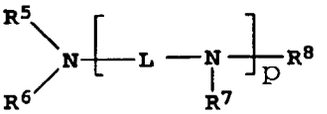
$$R_1N(CH_2PO_3M_2)_2$$

or the structure (II):

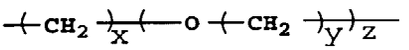
$$R_2R_3C(PO_3M_2)_2$$

wherein
R_1 is hydrogen, an alkyl group of 1 to 12 carbon atoms, an alkylaminoalkyl group wherein each alkyl has 1 to 12 carbon atoms, an alkoxyalkyl group of 1 to 12 carbon atoms, an aryl group having 6 to 10 carbon atoms in the ring, a cycloalkyl group having 5 to 10 carbon atoms in the ring, or a heterocyclic group having 5 to 10 atoms in the ring,
R_2 is hydrogen, an alkyl group of 1 to 12 carbon atoms, an aryl group having 6 to 10 carbon atoms in the ring, a cycloalkyl group having 5 to 10 carbon atoms in the ring, a heterocyclic group having 5 to 10 atoms in the ring, $-PO_3M_2$ or $-CHR_4PO_3M_2$,
R_3 is hydrogen, hydroxyl, an alkyl group of 1 to 12 carbon atoms or $-PO_3M_2$,
R_4 is hydrogen, hydroxyl, an alkyl group of 1 to 12 carbon atoms or $-PO_3M_2$, and

M is hydrogen or a water-soluble monovalent cation, and
the tertiary aminocarboxylic acid has the structure (III)



wherein R^5, R^6, R^7 and R^8 are independently a hydroxyalkyl group or a carboxyalkyl group, provided at least one of them is a carboxyalkyl group, p is 0, 1, 2 or 3, L is an alkylene group, a



group, a cyclic alkylene group having 6 carbon atoms in the ring or an arylene group having 6 to 10 carbon atoms in the ring, x and y are independently integers of 2 to 4, and z is an integer of 1 to 3, or a salt of the tertiary aminocarboxylic acid.

3. The solution as claimed in either of claims 1 or 2 wherein the organic phosphonic acid or salt thereof is 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid or diethylenetriamine-N,N,N',N",N"-penta(methylenephosphonic acid), and the tertiary aminocarboxylic acid is diethylenetriaminepentaacetic acid or 2-hydroxypropylenediaminetetraacetic acid, present in an amount of from 0.0001 to 0.012 mol/l.

4. The solution as claimed in any of claims 1 to 3 having a pH of from 10 to 11, and
wherein the bleaching agent is hydrogen peroxide present in an amount of at least 0.15 mol/l.

5. The solution as claimed in any of claims 1 to 4 comprising the chloride ions in an amount of from 0.45 to 1 mol/l.

6. A method for processing a color silver halide photographic element comprising:
bleaching an imagewise exposed and developed color silver halide photographic element containing a silver halide emulsion, with the hydrogen peroxide bleaching solution as claimed in any of claims 1 to 5.

7. The method as claimed in claim 6 wherein

the photographic element is a color negative film and the hydrogen peroxide bleaching agent is present in an amount of from 0.9 to 3 mol/l,
the photographic element is a motion picture print film and the hydrogen peroxide bleaching agent is present in an amount of from 0.15 to 1 mol/l, or
the photograhpic element is a photographic paper and the hydrogen peroxide bleaching agent is present in an amount of from 0.15 to 3 mol/l.

8. The method as claimed in either claim 1 or 2 wherein silver chloride is present in the silver halide emulsion at from 0 to 90 mol %.

9. The method as claimed in any of claims 6 to 8 wherein the silver halide emulsion contains 90 mol % or more of silver chloride.

10. The method as claimed in any of claims 6 to 9 wherein the photographic element comprises a silver level of less than 1 g/m^2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0444

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)
Y	US-A-4 301 236 (IDOTA YOSHIO ET AL) 17 November 1981 * column 7, line 43 - line 55; claims 1,7 * ---	1-10	G03C7/42 D06L3/02
D,Y	EP-A-0 428 101 (FUJI PHOTO FILM CO LTD) 22 May 1991 * page 3, line 1 - line 55; claims 1,3,4 * ---	1-10	
D,A	WO-A-92 07300 (KODAK LTD ;EASTMAN KODAK CO (US)) 30 April 1992 * claim 3 * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C
D06L
D21C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 June 1996	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)