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

(11) Publication number: **0 530 921 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **92202662.0**

(51) Int. Cl.[5]: **G03C 7/413**

(22) Date of filing: **03.09.92**

(30) Priority: **06.09.91 US 755973**

(43) Date of publication of application:
10.03.93 Bulletin 93/10

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL PT SE

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(54) **Photographic color developer formulation using an alpha amino acid for enhanced solution stability.**

(57) Photographic color developing compositions containing an alpha amino acid as sole developer preservative, optionally in combination with N,N-dialkylhydroxylamine or an alkanolamine.

EP 0 530 921 A1

This invention pertains to novel compositions and methods for processing photographic color elements. More specifically, this invention relates to novel photographic color developing compositions and to a method of processing photographic elements utilizing such developing compositions.

The formation of color photographic images by the image-wise coupling of oxidized primary aromatic amino developing agents with color forming or coupling compounds to form indoaniline, indophenol, and azomethine dyes is well known. In these processes, the subtractive process of color formation is ordinarily used, and the image dyes customarily formed are cyan, magenta, and yellow, the colors that are complementary to the primary colors, red, green, and blue, respectively. Usually phenol or naphthol couplers are used to form the cyan dye image, pyrazolone or cyanoacetyl derivative couplers are used to form the magenta dye image, and acylacetamide couplers are used to form the yellow dye image.

In these color photographic systems, the color-forming coupler may be either in the developer solution or incorporated in the light-sensitive photographic emulsion layer, so that during development, it is available in the emulsion layer to react with the color developing agent that is oxidized by silver image development. Diffusible couplers are used in color developer solutions. Nondiffusing couplers are incorporated in photographic emulsion layers. When the dye image formed is to be used *in situ*, couplers are selected which form non-diffusing dyes. For image transfer color processes, couplers are used which will produce diffusible dyes capable of being mordanted or fixed in the receiving sheet.

It is common practice in the photographic art to include a chemical for the purpose of retarding aerial oxidation of the color developing agent. Hydroxylamines and sulfite salts have both been used for this purpose. However, both have their disadvantages.

The amount of sulfite which can be tolerated in the developer solution is limited by the fact that sulfite competes with couplers for oxidized developing agent and thereby adversely affects dye formation. Typically, yellow dye-forming couplers react with oxidized developing agent more slowly than cyan or magenta dye-forming couplers so that the competition between coupler and sulfite has the greatest adverse effect on the formation of the yellow dye image.

Use of hydroxylamine, or a water-soluble acid salt thereof, is disadvantageous since it tends to act as a scavenger which reduces oxidized color developing agent before it can react with a coupler to form a dye. It also acts as a developing agent which competes with the color developing agent unless it is adequately restrained. Some hydroxylamines have a characteristic amine odor and are volatile.

Amino acids have previously been used in color developer solutions. U.S. Patent 4,273,863 discloses employing amino acids as building blocks to synthesize larger molecules for use as preservatives in combination with the developing agent, hydroquinone. U.S. Patent 4,189,319 discloses using the amino acid, arginine, as a development accelerator. U.S. Patent 4,124,391 discloses using monosaccharides to protect against aerial oxidation either alone or in combination with an amino acid. U.S. Patent 4,833,068 discloses using the combination of an hydroxylamine and iminodiacetic acid to retard oxidation. U.S. Patent 4,170,478 discloses using an unsubstituted or monosubstituted hydroxylamine in combination with an amino acid, alkanolamine, or ortho- or para- aminobenzoic acid in a low- or no-sulfite system to prevent aerial oxidation.

None of the aforementioned references, however, disclose utilizing an alpha amino acid as the exclusive developer preservative in a color developing solution. Utilizing an alpha amino acid as the sole developer preservative in color developing compositions complies with current trends in the photographic industry which favor processing solutions that are stable, odorless, and environmentally safe.

There has thus been a need for photographic color developing compositions resistant to aerial oxidation, containing developer preservatives that are stable, odorless, and environmentally safe. There has also been a need for improved development methods characterized by retardation of the aerial oxidation of a primary aromatic amino color developing agent.

These needs have been satisfied by providing a photographic color developing composition comprising a primary aromatic amino color developing agent and an alpha amino acid as sole developer preservative. The inventive photographic color developing composition can further include an alkanolamine and an N,N-dialkylhydroxylamine as a second developer preservative.

There has also been provided a method of retarding aerial oxidation of a primary aromatic amino color developing agent in a photographic color developing solution comprising the step of incorporating in the solution an alpha amino acid as sole developer preservative.

There has further been provided a method of color developing a photographic element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, which comprises the step of contacting the element with a color developing composition as described above.

Additionally there has been provided a method of rapid access processing of a silver halide photographic color element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, which comprises the steps of: contacting said element with a color developing composition as defined above; bleach-fixing the element without washing between the developing and bleach-fixing steps; and stabilizing the element without washing between the bleach-fixing and stabilizing steps.

Also, there has been provided a method of processing a chlorobromide or all-chloride silver halide photographic element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, comprising the steps of contacting the element with a prebath; rinsing the element; contacting the element with a color developing composition as defined above; contacting the element with a stop bath; washing the element; optionally fixing the element followed by washing the element; bleaching the element; washing the element; fixing the element; washing the element; and rinsing the element.

It has now been discovered that photographic color developer compositions containing a primary aromatic amino color developing agent can be protected against aerial oxidation by the use of an alpha amino acid exclusively. It has been determined that glycine and threonine in particular provide superior developer preservative protection to color developing compositions.

Further, it has now been discovered that an alpha amino acid in combination with an alkanolamine or an N,N-dialkylhydroxylamine provides an additional improvement in developer preservative protection to color developing compositions.

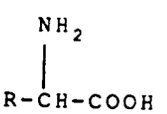
The novel photographic color developing compositions of this invention are especially useful with high-chloride silver halide emulsions. They are free of or at least substantially free of bromide, since bromide in significant quantities can unduly restrain the development reaction. They are free of or contain low concentrations of sulfite to minimize competition with the dye forming reactions.

In a preferred embodiment of the invention, the aforesaid photographic color developing composition is free of benzyl alcohol and is used in a rapid access process for processing silver halide photographic emulsions, for example high-chloride silver halide photographic color elements. Said rapid access process comprises the steps of color developing, bleach-fixing without washing between the color developing and bleach-fixing steps, and stabilizing without washing between the bleach-fixing and stabilizing steps. Elimination of the benzyl alcohol from the developing composition allows the bleach-fix to be utilized at a lower pH than is otherwise permissible, without the risk of producing leuco cyan dye. The low pH increases the rate of bleach-fix reactions, thereby enabling the use of a short bleach-fix time as is needed for a rapid access process.

As used herein, "high chloride" denotes a silver chloride content of at least about 75%, preferably at least 90%, on a molar basis. However, it should be noted that the process is not limited to such emulsions, but can also be used with emulsions having a lower silver chloride content.

In another preferred embodiment of the invention, the aforesaid photographic color developing composition is used in a method of developing a chlorobromide or all-chloride silver halide photographic element, which comprises the sequential steps of contacting the element with a prebath, a rinse, a color developing composition as defined above, a stop bath, a wash, an optional fixing bath and a second wash, a bleaching bath, another wash, a fixing bath, another wash, and a final rinse.

As described hereinabove, the novel color developer compositions according to the invention comprise an alpha amino acid which functions to retard the aerial oxidation of the developing agent. It is represented by the formula I:



I

wherein R is, for example, H, an alkyl group, an alkaryl group, or another substituent. Examples include glycine, alanine, leucine, serine, threonine, valine and isoleucine. Glycine and threonine are particularly preferred alpha amino acids. Other alpha amino acids are also encompassed within the invention.

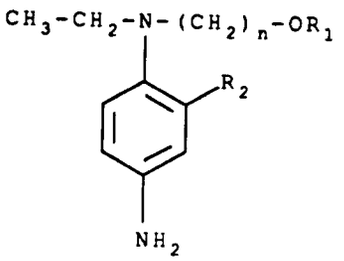
The primary aromatic amino color developing agents that are utilized in the compositions and methods of this invention are well known and widely used in a variety of color photographic processes. They include aminophenols and p-phenylenediamines. They are usually used in the salt form, such as the hydrochloride or sulfate, as the salt form is more stable than the free amine. The agents are generally employed in

concentrations of from 0.1 to 20 grams per liter (g/l) of developing solution and more preferably from 0.5 to 10 g/l of developing solution.

Examples of amino phenol developing agents include o-aminophenol, p-aminophenol, 5-amino-2hydroxytoluene, 2-amino-3-hydroxytoluene, 2-hydroxy-3-amino-1,4-dimethylbenzene, and the like.

Particularly useful primary aromatic amino color developing agents are the p-phenylenediamines, and especially the N,N-dialkyl-p-phenylenediamines in which the alkyl groups or the aromatic nucleus can be substituted or unsubstituted. Examples of useful p-phenylenediamine color developing agents include: N,N-diethyl-p-phenylenediamine monohydrochloride; 4-N,N-diethyl-2-methylphenylenediamine monohydrochloride; 4-(N-ethyl-N-2methanesulfonylaminoethyl)-2-methyl-phenylenediamine sesquisulfate monohydrate; 4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine sulfate; 4-N,N-diethyl-2,2'-methanesulfonylaminoethylphenylenediamine hydrochloride, and the like.

An especially preferred class of p-phenylenediamine developing agents are those containing at least one alkylsulfonamidoalkyl substituent attached to the aromatic nucleus or to an amino nitrogen. Other classes of p-phenylenediamines are the 3-alkyl-N-alkyl-N-alkoxyalkyl-p-phenylenediamines and the 3-alkoxy-N-alkyl-N-alkoxyalkyl-p-phenylenediamines. These developing agents are described in U.S Patents 3,656,950 and 3,658,525 and can be represented by the formula II:



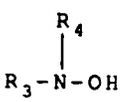
II

wherein n is an integer from 2 to 4, R_1 is an alkyl group of from 1 to 4 carbon atoms, and R_2 is an alkyl group of from 1 to 4 carbon atoms or an alkoxy group of from 1 to 4 carbon atoms. Illustrative examples of these developing agents include the following compounds: N-ethyl-N-methoxybutyl-3-methyl-p-phenylenediamine, N-ethyl-N-ethoxyethyl-3-methyl-p-phenylenediamine, N-ethyl-N-methoxyethyl-3-n-propyl-p-phenylenediamine, N-ethyl-N-methoxyethyl-3-methoxy-p-phenylenediamine, N-ethyl-N-butoxyethyl-3-methyl-p-phenylenediamine, and the like.

The photographic color developing compositions of this invention are employed in the form of aqueous alkaline working solutions having a pH of 10 and most typically in the range of from 9 to 13. To provide the necessary pH, the compositions include one or more of the well-known and widely used pH buffering agents, such as the alkali metal carbonates or phosphates. Potassium carbonate is especially useful as a pH buffering agent.

A further ingredient that optionally can be added is an N,N-dialkylhydroxylamine. The N,N-dialkylhydroxylamine can be used in the color developing composition in the form of the free amine, but can also be employed in the form of a water-soluble acid salt. Examples of such salts are sulfates, oxalates, chlorides, phosphates, carbonates, acetates, and the like.

The N,N-dialkylhydroxylamine is preferable of the formula III:

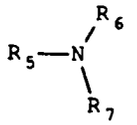


III

wherein R_3 and R_4 represent the same or different alkyl groups of 1 to 4 carbon atoms.

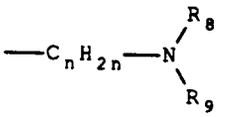
Exemplary N,N-dialkylhydroxylamines include: N,N-diethylhydroxylamine, N-ethyl-N-methylhydroxylamine, N-ethyl-N-propylhydroxylamine, N,N-dipropylhydroxylamine, N-methyl-N-butylhydroxylamine, and the like.

A further ingredient which optionally can be included in the color developing composition is an alkanolamine. The alkanolamines are primarily useful in providing additional protection against oxidation. As described in Case et al., U.S. Patent 4,170,478 preferred alkanolamines for use in photographic color developing compositions are compounds of the formula IV:



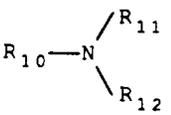
IV

wherein R_5 is an hydroxyalkyl group of 2 to 6 carbon atoms, and R_6 and R_7 individually are a hydrogen atom, an alkyl group of 1 to 6 carbon atoms, an hydroxyalkyl group of 2 to 6 carbon atoms, a benzyl radical, or a group according to the formula V:



V

wherein n is an integer from 1 to 6, and R_8 and R_9 individually are a hydrogen atom, an alkyl group of 1 to 6 carbon atoms or an hydroxylalkyl group of 2 to 6 carbon atoms. Alkanolamines which are especially preferred are compounds of the formula VI:



VI

wherein R_{10} is an hydroxylalkyl group of 2 to 4 carbon atoms, and R_{11} and R_{12} are individually an alkyl group to 1 to 4 carbon atoms or an hydroxyalkyl group of 2 to 4 carbon atoms. Typical examples of alkanolamines which can be used in the color developing compositions according to the invention include: ethanolamine, diethanolamine, triethanolamine, di-isopropanolamine, 2-methylaminoethanol, 2-ethylaminoethanol, 2-dimethylaminoethanol, 2-diethylaminoethanol, 1diethylamino-2-propanol, 3-diethylamino-1-propanol, 3-dimethylamino-1-propanol, isopropylaminoethanol, 3-amino-1-propanol, 2-amino-3-methyl-1,3-propanediol, ethylenediamine tetraisopropanol, benzyldiethanolamine, 2-amino-2-(hydroxymethyl)-1,3-propanediol, and the like.

The color developing compositions utilized in the method according to the invention typically contain one or more sequestering agents, for example, an aminopolycarboxylic acid chelating agent or an aminopolyphosphonic acid chelating agent.

Typical examples of the aminopolycarboxylic acid chelating agents include: nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), 1,3-diamino-2-propanol-N,N,N,N-tetraacetic acid (DPTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethylethylenediaminetriacetic acid, cyclohexanediaminotetraacetic acid, aminomalonic acid, and the like.

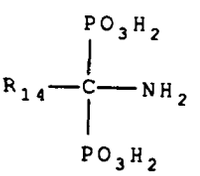
Among the useful aminopolyphosphonic acid chelating agents are the following:

amino-N,N-dimethylenephosphonic acids of the formula VII:

R_{13}-N($CH_2PO_3X_2$)$_2$ VII

wherein X is a hydrogen atom or a monovalent cation and R_{13} is an alkyl group, an aryl group, an aralkyl group, an alkaryl group, an alicyclic group or a heterocyclic radical, all of which can be further substituted with substituents such as hydroxyl, halogen, an alkoxy group, a PO_3X_2 group, a $CH_2PO_3X_2$ group, or an N-($CH_2PO_3X_2$)$_2$ group;

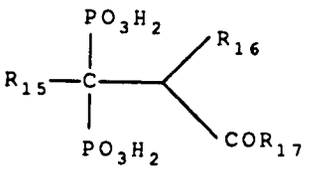
aminodiphosphonic acids of the formula VIII:



VIII

in which R_{14} is an alkyl group, preferably of one to five carbon atoms; and

N-acylaminodiphosphonic acids of the formula IX:



IX

where R_{15}, R_{16} and R_{17} are hydrogen or an alkyl group, preferably alkyl of one to five carbon atoms.

Typical examples of the aminopolyphosphonic acid chelating agents useful in the novel color developing compositions according to the invention include: 1-aminoethane-1,1-diphosphonic acid, 1-aminopropane-1,1-diphosphonic acid, N-acetyl-1-aminoethane-1,1-diphosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, 1,2-cyclohexanediamine-N,N,N,Ntetramethylenephosphonic acid, o-carboxyanilino-N,N-dimethylenephosphonic acid, propylamino-N,N-dimethylenephosphonic acid, 4-(N-pyrrolidino) butylamine-N,N-bis-methylenephosphonic acid, 1,3-diaminopropanol-N,N,N,N-tetramethylenephosphonic acid, 1,6-hexanediamine-N,N,N,N-tetramethylenephosphonic acid, o-acetamidobenzylamino-N,N-dimethylenephosphonic acid, o-toluidine-N,N-dimethylenephosphonic acid, 2-pyridylamino-N,N-dimethylenephosphonic acid, diethylenetriamine pentamethylenephosphonic acid, and the like.

Additional ingredients which can optionally be included in the photographic color developing compositions include thickening agents, brightening agents, wetting agents and so forth.

It is particularly preferred that the photographic color developing compositions of this invention be free of benzyl alcohol.

Development of photographic elements in accordance with the method described herein can be advantageously employed in the processing of photographic elements designed for the reversal color processing or in the processing of negative color elements or color print materials. The photosensitive layers can contain conventional addenda and be coated on any of the photographic supports, such as, for example, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terephthalate film, paper, polymer-coated paper and the like.

The invention is further illustrated by the following examples, without being limited thereby.

Example 1

The photographic color developing solution shown below will be referred to as Developer 1.

Component	Concentration
Lithium salt of sulfonated polystrene (30% by weight aqueous solution)	0.25 mL/L
Triethanolamine	11.0 g/L
KODAK EKTRAPRINT 2 Stain-Reducing agent (a substituted triazinylstilbene)	2.3 g/L
Lithium sulfate	2.7 g/L
KODAK ANTI-CALCIUM #5(1-hydroxyethylidene-1-diphosphonic acid)	0.8 ml/L
Potassium chloride	1.8 g/L
Potassium bromide	0.2 g/L
4-(N-ethyl-N-2-methanesulfonylamidoethyl)-2-methylphenylenediamine sesquisulfate monohydrate	4.85 g/L
Potassium carbonate	25.0 g/L
Water to one liter pH = 10.12	

To evaluate color developer solution stability, the concentration of the p-phenylenediamine developing agent was measured over time and the decomposition rate calculated as p-phenylenediamine (PPD)/ time in units of g/L/week.

Developing Solution	Decomposition Rate (g/l/week)
Developer 1	0.47
Developer 1 + 5.18 g/l Glycine	0.11
Developer 1 + 6.15 g/l Alanine	0.35
Developer 1 + 12.02 g/l Arginine	0.33
Developer 1 + 9.18 g/l Aspartic Acid	0.32
Developer 1 + 10.15 g/l Glutamic Acid	0.31
Developer 1 + 9.05 g/l Leucine	0.33
Developer 1 + 7.25 g/l Serine	0.29
Developer 1 + 8.22 g/l Threonine	0.13
Developer 1 + 8.08 g/l Valine	0.35
Developer 1 + 10.70 g/l Histidine	0.35
Developer 1 + 7.94 g/l Proline	0.37
Developer 1 + 14.08 g/l Tryptophan	0.29

The above rates show that the addition of an amino acid gave a developer with enhanced stability as compared with Developer 1.

Example 2

A photographic color print material of the high chloride type, as described in U.S. Patent 4,269,927 (May 26, 1981, to Atwell) was processed in a three-step process consisting of 45 sec. development, 45 sec. bleach-fix and 90 sec. wash steps. Each step was carried out at 35° C. The print material was then dried. Results for Developer 1 + 5.18 g/l glycine in comparison to Developer 1 alone are summarized below as percent change.

Quantity	% Change
Dmin R	0
Dmin G	0
Dmin B	0
Dmax R	1.8%
Dmax G	1.8%
Dmax B	2.5%
Speed R	1.5%
Speed G	1.2%
Speed B	1.1%

The above results show that the addition of glycine to the developer does not significantly affect the photographic results. It does not perform as an accelerator, affect fog or change speed.

Example 3

The following compositions were prepared and their decomposition rates were determined.

Developing Composition	Decomposition Rate (g/l/week)
Developer 1 + 5.18 g/l Glycine	0.08
Developer 1 + 2.6 g/l Glycine plus 4.0 ml/l N,N-Diethylhydroxylamine	0.05
Developer 1 + 5.18 g/l Glycine minus Triethanolamine	0.09
Developer 1 + 5.18 g/l Glycine minus KODAK Anti-calcium #5	0.10
Developer 1 + 5.18 g/l Glycine minus Triethanolamine and minus KODAK Anti-calcium #5	0.14

The above results show that the addition of the triethanolamine or the sequestering agent has no appreciable effect on decomposition rate.

Example 4

The photographic color developing solution shown below will be referred to as Developer 2.

Component	Concentration
Diethylenetriaminepentaacetic acid, Na salt, 40% in water	7.0 ml/l
Potassium chloride	3.1 g/l
Potassium bromide	0.1 g/l
Diethylamino-ortho-toluidine hydrochloride	2.8 g/l
Sodium carbonate	21.0 g/l
Water to make 1 liter pH to 10.55	

Developer Solution	Decomposition Rate (g/l/week)
Developer 2	0.39
Developer 2 + 3.9 g/l Glycine	0.12

The above rates show that glycine is again an effective preservative.

It is to be understood that the foregoing detailed description and specific examples, while indicating preferred embodiments of the present invention, are given by way of illustration and not limitation. Many changes and modifications within the scope of the present invention may be made without departing from the spirit thereof, and the invention includes all such modifications.

Claims

1. A photographic color developing composition comprising:
(a) a primary aromatic amino color developing agent; and
(b) an alpha amino acid as sole developer preservative.

2. A photographic color developing composition as claimed in claim 1, wherein said alpha amino acid is glycine, alanine, leucine, serine, threonine, valine or isoleucine.

3. A photographic color developing composition as claimed in claim 1 or 2, wherein said developing agent is a p-phenylenediamine or an aminophenol.

4. A photographic color developing composition as claimed in any of claims 1 to 3, further comprising a sequestering agent.

5. A photographic color developing composition as claimed in claim 7, wherein said sequestering agent is an acid chelating agent selected from an aminopolycarboxylic acid chelating agent, an aminopolyphosphonic acid chelating agent, or a mixture thereof.

6. A photographic color developing composition as claimed in any of claims 1 to 5 which is substantially free of benzyl alcohol.

7. A photographic color developing composition as claimed in any of claims 1 to 6 which is substantially free of sulfite ions.

8. A photographic color developing composition as claimed in any of claims 1 to 7, further comprising an alkanolamine or an N,N-dialkylhydroxylamine as a second developer preservative.

9. A method of retarding aerial oxidation of a primary aromatic amino color developing agent in a photographic color developing solution comprising an alpha amino acid as defined in claim 1 or 2 as sole developer preservative.

10. A method of developing a color image in a photographic element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, which comprises the step of contacting said element with a color developing composition as claimed in any of claims claim 1 to 8.

11. A method of rapid access processing of a silver halide photographic color element comprising a support and a silver halide emulsion containing an imagewise distribution of developable silver halide grains, which comprises the steps of:
(a) contacting said element with a color developing composition as claimed in any of claims 1 to 8;
(b) bleaching and fixing or bleach-fixing said element; and
(c) stabilizing said element,
with optional washing steps between each processing step.

12. A method of processing a photographic element as claimed in claim 10 or 11 in which the silver halide layers of the photographic element comprise chlorobromide or all-chloride.

13. A method as claimed in claim 12, said element is treated with a stop bath.after the development step and fixed and subsequently washed before the bleach or bleach-fix step.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2662

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.5)
A	EP-A-0 285 010 (FUJI PHOTO FILM CO., LTD) 5 October 1988 * page 3, line 14 - page 4, line 8 * * page 18, line 1 - page 19, line 55 * * page 29, line 1 - page 35, line 59 * * page 37, line 11 - page 37, line 27 * * examples 1-18 * * claims 1-14 *	1-7,9	G03C7/413
X	* page 3, line 14 - page 4, line 8 * * page 18, line 1 - page 19, line 55 * * page 29, line 1 - page 35, line 59 * * page 37, line 11 - page 37, line 27 * *page78 - 79, compositions 11 - 15 ---	8,10, 11-13	
A,D	FR-A-2 394 113 (EASTMAN KODAK COMPANY) 5 January 1979 * page 1, line 6 - page 7, line 1 *	1-7,9	
X,D	* page 1, line 6 - page 7, line 1 * * example 3 * -----	8,10-13	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	12 NOVEMBER 1992	MARKOWSKI V.F.

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

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