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

(11) Publication number : **0 689 091 A1**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **95420137.2**

(22) Date of filing : **26.05.95**

(51) Int. Cl.^{6} : **G03C 1/34**, G03C 1/015, G03C 1/10

(30) Priority : **09.06.94 FR 9407275**

(43) Date of publication of application :
27.12.95 Bulletin 95/52

(84) Designated Contracting States :
DE FR GB

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(54) Process for preparing a silver halide photographic emulsion sensitised in the presence of hydroquinone derivatives

(57) The present invention concerns a silver halide photographic emulsion, particularly a silver halide emulsion sensitised by means of a novel combination of sensitising compounds, and the process which enables such an emulsion to be obtained.

According to the invention, the emulsion is chemically sensitised by means of a compound of sulphur and/or gold and/or selenium and at least one reducing compound under particular conditions of pH.

This emulsion enables the sensitivity of a silver halide emulsion to be increased without changing the fogging level.

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The present invention concerns a silver halide photographic emulsion, and particularly a silver halide emulsion sensitised by means of a novel combination of sensitising compounds, and the process for obtaining such an emulsion.

In the field of photography, it is known that chemical compounds can be added to silver halide emulsions in order to increase their sensitivity. These compounds enable centres of chemical sensitivity to be formed at the surface and/or inside the silver halide grains. These centres of sensitivity are generated by two totally different processes, sensitisation by reduction (the formation of seeds of metallic silver) and sensitisation by sulphuration (the formation of silver sulphide).

The sensitisation of the emulsions is limited by the quantity of sensitising compounds which can be added to the emulsion without causing a significant increase in fogging.

Hydroquinone and derivatives of hydroquinone are known for their silver halide reducing properties. They are usually used in photographic processing as photographic product developing substances. Derivatives of particular interest for this type of application are described in Chimie et Physique Photographiques, Glafkides, page 154, and in a large number of patents such as US patent 4 377 634.

Hydroquinone derivatives can also be incorporated into a photographic product. For example, US patent 4 614 707 describes a colour reversible photographic product which comprises several layers of silver halide emulsion, each of these layers containing a dye-forming coupler. These photosensitive layers are separated by intermediate layers comprising silver halides which do not participate in the formation of the image, and at least one of these intermediate layers contains a hydroquinone derivative substituted by a sulpho, carboxyl, sulphoalkyl or carboxyalkyl group.

European patent 209 010 describes a high-contrast negative photographic product obtained using a monodisperse emulsion consisting of silver halide grains with a size of less than 0.7 μm and which are such that the latent image forms on the surface of these grains. This emulsion also comprises an arylhydrazide contrast amplifier and a quantity of a hydroquinone derivative for reducing sensitivity to pressure.

US patent 3 192 146 describes a silver halide photographic emulsion sensitised by a novel combination of chemical sensitisers which comprises a thioether and a hydroquinone derivative associated with a compound capable of salting out or forming bisulphite ions. Such a combination enables the sensitivity of a silver halide photographic emulsion to be increased.

It is known in photographic technology that the pH value used in the precipitation of emulsions, in emulsion sensitization or in the layering of photographic emulsions, greatly influences the characteristics of the photographic emulsion. The pH conditions strongly influence the sensitometric properties, in particular the fogging level.

The object of the present invention is to increase the sensitivity of a silver halide emulsion without changing the fogging level, by associating a conventional chemical sensitisation using sulphur, gold or selenium with a sensitisation by reduction by means of a polyhydroxybenzene under particular pH conditions.

The present invention resolves the problem related to the increase in fogging level when sensitisation by reduction is used.

The present invention concerns a silver halide photographic emulsion chemically sensitised by means of a sensitiser chosen from among sulphur, gold and selenium and at least one reduction sensitiser characterized in that the reduction sensitiser is a polyhydroxybenzene, and in that the pH of the emulsion after the addition of the different chemical sensitisers is between 7 and 10.

The polyhydroxybenzene according to the present invention is preferably a hydroquinone derivative.

The hydroquinone derivatives are, for example, 2-(2'-octodecyl)-5-sulphohydroquinone, 2,5-didodecylhydroquinone, 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone or a salt of these compounds. These hydroquinone derivatives can be used alone or in combination.

The quantities of hydroquinone derivatives may be between 0.05 and 1 mmole per mole of silver, and preferably between approximately 0.1 and 0.6 mmole per mole of silver.

According to one embodiment of the invention, the hydroquinone derivative is 2-(2'-octodecyl)-5-sulphohydroquinone and the pH of the emulsion is between 7 and 9 and preferably 8 and 9.

The compounds of sulphur and/or gold and/or selenium which are used for chemically sensitising the emulsion of the invention are conventional compounds such as thiosulphates, thioureas, aurous sulphocyanide, aurothiocyanates, selenoureas, etc. These compounds were described, for example, in Research Disclosure No 308119, December 1989, Section III.

The quantities of chemical sensitisers containing sulphur, gold or selenium added to the emulsion are determined experimentally in order to obtain an optimally sensitised emulsion.

The process for preparing such emulsions is comprised of precipitating silver halide grains in a colloid using a solution of silver nitrate and one or more halide salts, and then adding one or more spectral sensitising dyes in order to sensitise the emulsion by one or more chemical sensitising compounds containing sulphur and/or gold and/or selenium and at least one polyhydroxybenzene such as, for example, a hydroquinone derivative.

After the addition of the spectral and chemical sensitising dyes, the pH of the emulsion is adjusted to a value lying between 7 and 10.

According to one embodiment of the invention, the spectral sensitising dye or dyes, the chemical sensitising dye or dyes containing sulphur and/or gold and/or selenium and the hydroquinone derivative or derivatives are added to the emulsion in that order. The pH is then adjusted by adding a strong base, for example sodium hydroxide.

According to one embodiment, after the pH has been adjusted to a value lying between 7 and 10 by adding a strong base, the temperature of the sensitised emulsion is raised to between 30 and 90°C and preferably above 50°C, in order to obtain a better adsorption of the different sensitisers. In general, a level stage is maintained at a temperature of around 60°C.

The photographic emulsion may consist of one or more silver halides chosen from amongst silver chloride, bromide and iodide.

The silver halide grains may have different morphologies, for example tabular, octahedral (faces 111), cubo-octahedral or cubic (faces 100).

The silver halide emulsion may be spectrally sensitised with conventional spectral sensitising dyes as described for example in Research Disclosure, December 1989, No 308119, Section IV (hereinafter referred to as Research Disclosure).

These dyes are, for example, cyanine, merocyanine or hemioxodol dyes.

Although the quantity of each of the spectral sensitisers differs greatly according to the conditions of use, the quantity of spectral sensitisers is preferably between 0 and 1.4 mmole per mole of silver.

The emulsions of the present invention may be used in black and white or colour photographic products of different types, such as negative, positive or reversal photographic products.

When these photographic products are colour photographic products, they comprise, in a conventional manner, at least three components which are respective blue, green and red sensitive, providing respectively the yellow, magenta and cyan components of the subtractive synthesis of the colour image.

Colour photographic products generally comprise a support carrying at least one layer of blue-sensitive silver halide emulsion with which a yellow dye forming coupler is associated, at least one layer of green-sensitive silver halide emulsion with which a magenta dye forming coupler is associated, and at least one red-sensitive silver halide emulsion with which a cyan dye forming coupler is associated.

These products may contain other layers which are conventional in photographic products, such as spacing layers, filter layers and anti-halo layers. The support may be any suitable support used in photographic products. Conventional supports comprise polymer films, paper (including polymer-coated paper), glass and metal. Research Disclosure, Section XVII, provides details about supports and ancillary layers in photographic products.

The silver halide emulsions of the invention, and other layers on the photographic products of this invention, may contain, as a carrier, hydrophilic colloids, used alone or in combination with other polymer substances (for example latexes). Suitable hydrophilic substances comprise natural substances such as proteins, protein derivatives, cellulose derivatives (for example cellulose esters), gelatin (for example gelatin such as cattle bone or tanned gelatin treated by means of a base or gelatin such as pigskin gelatin treated with an acid), gelatin derivatives (for example acetylated gelatin, phthalylated gelatin, etc), polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar and albumin.

Surfactants can be incorporated in a layer of photographic emulsion or in another hydrophilic colloidal layer of the photographic product as a coating adjuvant, for example in order to prevent the accumulation of static charges, to improve lubrication properties, to improve the dispersion of the emulsion, to prevent adhesion, and/or to improve the sensitometric properties such as an increase in contrast or the sensitisation or acceleration of development.

The photographic emulsion of the present invention may contain dye image forming couplers, that is to say compounds capable of reacting with an aromatic amine oxidation product (generally a primary amine) to form a dye. Non-diffusible couplers containing a ballast group are desirable. It is possible to use either couplers with four equivalents or couplers with two equivalents. In addition, it is possible to use couplers enabling the colours to be corrected, or couplers releasing a development inhibiter during development (referred to as DIR couplers).

The photographic products of the invention may contain, amongst other things, optical brighteners, anti-fogging compounds, tanning agents, stabilising agents or absorption and/or diffusion agents as described in Sections V, VI, VIII, XI, XII and XVI of the above-mentioned Research Disclosure.

The methods of adding these different compounds, and the coating and drying methods, are described in Sections XIV and XV of Research Disclosure.

The products of the invention, after being exposed, undergo photographic processing for developing the silver latent image and a colour image, in the presence of a coupler, which, in certain cases, may be incorporated in the photographic product.

Development takes place by means of a reducing compound which, by oxydo-reduction reaction, transforms the exposed silver halide grains into metallic silver grains. The oxidised form of the reducing compound then reacts with the coupler to form a dye.

These reducing compounds are chosen from amongst the aromatic primary amines such as paraphenylene diamines, aminophenols, etc. These compounds may be used alone or in a mixture, or with ancillary developers. This bath may, in addition, contain a stabiliser such as sulphites, a buffer such as carbonates, boric acid, borates or alkanolamines.

The following examples illustrate the invention and show that the emulsions according to the invention have improved sensitometric properties.

EXAMPLE 1

(I) Precipitation of the emulsion

Using the "double-jet" precipitation technique, an AgBr tabular grain emulsion was prepared as follows:

Under strong agitation in a 20 litre evaporating vessel containing an aqueous solution of gelatin, 0.15 moles of NaBr and a propylene oxyde ethylene oxyde anti-foaming agent, a step consisting of the nucleation of the grains was carried out at 45°C and with a pH of 1.8 and pAg of 9, by introducing, over 15 seconds by the double-jet method, a 0.6 M solution of $AgNO_3$ and a 0.6 M solution of NaBr.

After a waiting period, a growth was effected on the AgBr nuclei obtained. For this purpose, in the solution obtained previously and kept at 60°C, a 1.6 M solution of $AgNO_3$ was introduced by the double-jet method over 48 minutes, at a flow rate of the type a + bt (a and b being constants and t the time in minutes), and the flow rate of halide salt (NaBr, 1.7 M) was adjusted so that the pAg remains constant and equal to 9. In this way 2.2 moles of AgBr were precipitated.

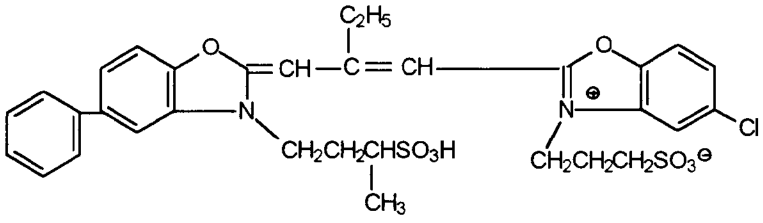
The emulsion was then cooled to 40°C. After washing of the emulsion, the pH was adjusted to 6.0 and the pAg to 8.

A pure tabular grain bromide emulsion was obtained, having an equivalent circular diameter of 2.0μm and a thickness of 0.11 μm.

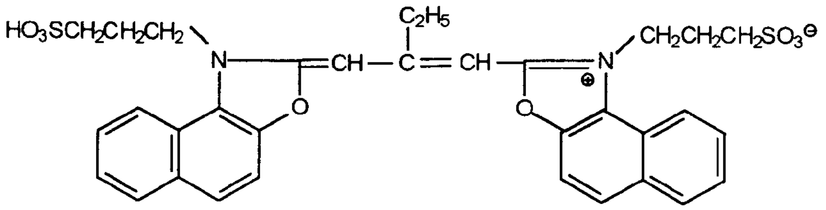
(II) Sensitisation of the emulsion

150 mg/mol of Ag of sodium thiocyanate, 0.612 mmoles per mole of Ag of the spectral sensitising dye (SI) and 0.204 mmol/mol of Ag of the spectral sensitising dye (SII), 6.3 mg/mol of Ag of sodium thiosulphate, 3.15 mg/mol of Ag of potassium tetrachloroaurate and 15 mg/mol of Ag of 3-methyl-1,3-benzothiazolium iodide were added to the emulsion obtained at (I) and which was maintained at 40°C.

The emulsion thus obtained was separated into four equal parts and each of the parts was treated in accordance with Table 1. The hydroquinone derivative used in this example was the sodium salt of [2-(2'-octadecyl)-5-sulphohydroquinone (D8N).



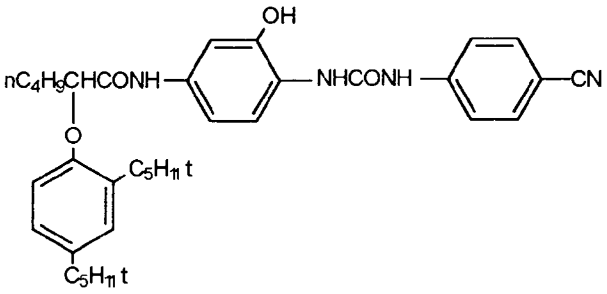
(SI)



(SII)

The temperature was increased to 65°C. This temperature was maintained for 15 min, and then the emulsions were cooled to 40°C.

The emulsions obtained were coated on a cellulose triacetate support with a silver content of 0.807 g/m², a gelatin content of 3.23 g/m² and a coupler (C1) in a proportion of 1.05 g/m². This layer of emulsion was covered with a top coating of gelatin (2.15 g/m²).



(CI)

The layer of emulsion was hardened using 1.75% bis(vinylsulphonyl)methane by weight of total gelatin.

The samples thus obtained were exposed by means of a Kodak® sensitometer fitted with a lamp with a colour temperature of 5500°K for 1/100 seconds. The sensitometer was fitted with a "Wratten 9®" filter which transmits light of a wavelength shorter than 460 nm.

The samples were then developed using a standard Kodak Flexicolor C41® process which comprises the following steps:

- development using a chromogenic developer,
- bleaching,
- first washing,
- fixing,
- second washing,
- stabilisation, and
- drying.

For each sample, the sensitivity of the sample was assessed by means of the formula:

$$\text{Sensitivity} = 100(1 - \log E)$$

where E represents the photographic exposure measured at the point of intersection between the tangent at maximum contrast and a straight line passing through the maximum density.

The minimum density (Dmin) is equal to the optical density of the support and of the fogging obtained without exposure. Although the value of the minimum density varies according to the use of the photographic product, it must in every case be less than or equal to 0.2.

The results obtained are set out in Table 1 below:

TABLE 1

	Emulsion		Sensitometry	
	D8N (mg/mol Ag)	pH	Dmin	Sens.
1-A (Ref)	0	6.5	0.038	100
1-B (Ref)	0	7.5	0.045	107
1-C (Ref)	0	8.5	0.052	111
1-D (Ref)	0	9.5	0.134	117
1-E (Ref)	0	10.5	0.837	110
1-I (Inv)	0.11	8.5	0.095	116
1-II (Inv)	0.22	8.5	0.091	117
1-III (Inv)	0.32	8.5	0.213	118
1-IV (Inv)	0.43	8.5	0.188	119
1-V (Inv)	0.11	9.0	0.11	116
1-VI (Inv)	0.22	9.0	0.12	115
1-VII (Comp)	0.11	10.5	1.101	107
1-VIII (Comp)	0.32	10.5	1.415	91

Examples 1A to 1E (reference) show that, when the pH of the emulsion is increased, an increase in sensitivity is observed which is inevitably accompanied by a not insignificant increase in the fogging level.

If, for example, Example 1-C and the examples of the invention 1-I, 1-II, 1-V and 1-VI are compared, it is seen that the addition of the hydroquinone derivative results in an increase in sensitivity compared with Examples 1-A to 1-E and a fogging level which remains lower than that obtained in Example 1-D, where the highest sensitivity was obtained.

The results of Examples 1-III and 1-IV show that, for a pH of around 8.5, when the quantity of hydroquinone derivative is greater than or equal to 0.32 mmol/mol Ag, the increase in sensitivity of the emulsion is accompanied by an increase in the fogging level greater than that of Example 1-D but which remains acceptable.

The comparative examples 1-VII and 1-VIII show that, for a pH of 10.5, the advantages of the present invention are no longer observed.

EXAMPLE 2

The emulsion was treated as described in Example 1 except that the hydroquinone derivative was 2.5-didodecylhydroquinone (IDH).

In this way the results in Table 2 were obtained.

In Examples 2-I to 2-V, the increase in sensitivity compared with the reference examples (without hydroquinone derivative) and a fogging level which always remains lower than that of Example 2-D, where the highest sensitivity was obtained, are observed as before.

TABLE 2

	Emulsion		Sensitivity	
	IDH mg/mol Ag	pH	Dmin	Sen.
2-A (Ref)	0	6.5	0.032	100
2-B (Ref)	0	7.5	0.037	105
2-C (Ref)	0	8.5	0.053	109
2-D (Ref)	0	9.5	0.135	109
2-E (Ref)	0	10.5	0.93	111
2-I (Inv)	0.11	8.5	0.082	110
2-II (Inv)	0.22	8.5	0.084	112
2-III (Inv)	0.33	8.5	0.085	112
2-IV (Inv)	0.45	8.5	0.099	112
2-V (Inv)	0.11	9.0	0.113	109
2-VI (Inv)	0.33	9.0	0.159	111

Example 2-VI shows that, when the pH is equal to 9, the quantity of hydroquinone derivative will preferably be less than 0.33 mmol/mol of Ag since, in this particular case, the fogging level is higher than in Example 2-D.

EXAMPLE 3:

The emulsion of Example 1 treated as described in Example 2 except that the hydroquinone derivative was 2,5 bis(1,1,3,3-tetramethylbutyl)hydroquinone (DOH).

In this way the results in Table 3 were obtained.

Examples 3-I to 3-V show that the addition of DOH at a pH of 8.5 or 9.0 enables the sensitivity of the emulsion to be increased compared with the reference emulsions without increasing the fogging level above that of Example 3-D, where the highest sensitivity was obtained.

TABLE 3

	Emulsion		Sensitivity	
	DOH mg/mol Ag	pH	Dmin	Sens.
3-A (Ref)	0	6.5	0.034	100
3-B (Ref)	0	7.5	0.038	104
3-C (Ref)	0	8.5	0.051	107
3-D (Ref)	0	9.5	0.132	107
3-E (Ref)	0	10.5	0.909	102
3-I (Inv)	0.15	8.5	0.077	108
3-II (Inv)	0.3	8.5	0.058	109
3-III (Inv)	0.45	8.5	0.062	110
3-IV (Inv)	0.60	8.5	0.062	110
3-V (Inv)	0.15	9.0	0.092	109
3-VI (Inv)	0.15	9.5	0.159	111
3-VII (Inv)	0.3	9.5	0.184	110
3-VIII (Inv)	0.45	9.5	0.201	110
3-IX (Inv)	0.60	9.5	0.274	109

In Examples 3-VI to 3-IX, a sensitivity is obtained which is greater than that obtained with Examples 3-A to 3-E and a fogging level higher than that obtained with these reference examples, but still acceptable.

In the particular case of DOH, a pH below 9.4 was preferably chosen.

Claims

1. Silver halide photographic emulsion chemically sensitised by means of sensitiser chosen from among sulphur, gold and selenium sensitiser and at least one reduction sensitiser, characterised in that the reduction sensitiser is a polyhydroxybenzene and in that the pH of the emulsion after the addition of the different chemical sensitisers is between 7 and 10.

2. Emulsion according to Claim 1, in which the polyhydroxybenzene is a hydroquinone derivative.

3. Emulsion according to Claim 1, in which the quantity of hydroquinone derivative is between 0.05 and 1 mmol/mol of Ag and preferably between 0.1 and 0.6 mmol/mol of Ag.

4. Emulsion according to Claim 1, in which the pH of the emulsion is between 7 and 9 and preferably 8 and 9.

5. Emulsion according to Claim 1 or 2, in which the hydroquinone derivative is chosen from amongst 2-(2'-octodecyl)-5-sulphohydroquinone, 2,5-didodecylhydroquinone, 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone or a salt of these compounds.

6. Emulsion according to Claim 5, in which the hydroquinone derivative is 2-(2'-octodecyl)-5-sulphohydroquinone and the quantity of this hydroquinone derivative is less than 0.3 mmol/mol of Ag.

7. Emulsion according to Claim 5, in which the hydroquinone derivative is 2,5-didodecylhydroquinone and the quantity of this hydroquinone derivative is less than 0.35 mmol/mol of Ag.

8. Emulsion according to Claim 5, in which the hydroquinone derivative is 2,5 bis(1,1,3,3-tetramethylbutyl)hydroquinone.

9. Silver halide photographic product consisting of a support and at least one layer of silver halide emulsion according to any one of the preceding Claims 1 to 8.

10. Process for preparing a photosensitive silver halide emulsion which is comprised of :

(1) precipitating silver halide grains in a colloid using a solution of silver nitrate and one or more halide salts,
(2) adding to the emulsion obtained at (1) one or more spectral sensitising dyes, one or more chemical sensitising compounds containing sulphur and/or gold and/or selenium and at least one polyhydroxybenzene,
(4) adjusting the pH of the emulsion obtained at (3) to a value above 7 and below 10, and
(5) optionally, effecting a heat treatment with a level stage at a temperature above 50°C.

11. Process according to Claim 10, in which the polyhydroxybenzene is a hydroquinone derivative.

12. Process according to Claim 10, in which the pH is adjusted to between 7 and 9 and preferably between 8 and 9.

13. Process according to Claim 11, in which the quantity of hydroquinone derivative is between 0.05 and 1 mmol/mol of Ag and preferably 0.1 to 0.6 mmol/mol of Ag.

14. Process according to Claim 11, in which the hydroquinone derivative is chosen from amongst 2-(2'-octodecyl)-5-sulphohydroquinone, 2,5-didodecylhydroquinone, 2,5-bis(1,1,3,3-tetramethylbutyl)hydroquinone or a salt of these compounds.

15. Process according to Claim 10, in which the hydroquinone derivative is as defined in any one of Claims 5 to 8.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 42 0137

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	GB-A-2 055 221 (E. I. DUPONT DE NEMOURS) * page 1, line 38 - line 44; claims; example 1 * ---	1-15	G03C1/34 G03C1/015 G03C1/10
Y	DE-B-12 07 792 (AGFA AKTIENGESELLSCHAFT) * the whole document * ---	1-15	
Y	DE-A-26 32 202 (FUJI PHOTO FILM) * claims 1,13; example 1 * ---	1-3, 9-11,13, 15	
Y	JOURNAL OF INFORMATION RECORDING MATERIALS, vol. 20, no. 3, December 1992 YVERDON CH, pages 197-239, GUNTHER FISCHER 'STABILISATOREN UND ANTISCHLEIERMITTEL FÜR PHOTOGRAPHISCHE SILBERHALOGENIDMATERIALIEN TEIL II: AROMATISCHE, ALIPHATISHE UND ANORGANISHE VERBINDUNGEN' * page 203, paragraph 3.10.4 - page 204 * ---	1-15	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)**
Y	FR-A-2 414 743 (KODAK-PATH) * page 7, line 3 - line 5; claims 1,2,6 * ---	1-15	G03C
Y	FR-A-2 538 135 (VEB FILMFABRIK WOLFEN) * page 4, line 12; claims 1,2; example 1 * ---	1-15	
Y	DE-A-20 34 064 (KONISHIROKU PHOTO INDUSTRY) * page 8, paragraph 2 - page 9, line 3; claims 1,6 * ---	1-15	
A	FR-A-2 208 133 (ILFORD) * page 10, line 8 - line 12; claim 1 * -----	6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 September 1995	Philosoph, L

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)