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(54) High sensitivity and developability multilayer color photographic material.

(57) The photographic characteristics of a photographic color material can be improved if a layer packet is used which includes, in the indicated order starting from the base and going outwards, at least one red-sensitive gelatin silver halide emulsion layer including cyan dye forming couplers, an intermediate layer including from 0.1 to 1 gram per square meter of a fine light insensitive gelatin silver halide emulsion and at least one green-sensitive gelatin silver halide emulsion layer including magenta-dye forming couplers associated with DIR compounds.

Croydon Printing Company Ltd.

High Sensitivity And Developability Multilayer Color Photographic Material.

Field Of The Invention

The present invention refers to a multilayer color photographic material and in particular to a multilayer color photographic material having high sensitivity and developability and good image quality.

Description Of The Prior Art

A multilayer color photographic material usually consists of a base having coated thereon a red-sensitive emulsion layer containing a cyan-dye forming coupler, a green-sensitive emulsion layer containing a magenta-dye forming coupler, a blue-sensitive emulsion layer containing a yellow-dye forming coupler, intermediate layers, filter layers, an antihalation layer and a protective layer.

It is strongly desired to obtain multilayer color photographic materials having high sensitivity and good image quality. Normally, high sensitivity and good image quality cannot be obtained together, since high sensitivity is obtained by increasing the dimensions of the silver halide grains and this causes an increase of image granularity. The use of compounds which during development release a development-inhibiting compound (the so-called DIR compounds), as described in US patents 3,227,554 and 3,773,201, causes a decrease of such granularity and it is therefore usual to employ such compounds in high-sensitivity photographic materials.

The use of a fine, light insensitive silver halide emulsion in combination with DIR compounds has been described in

US patents 3,892,572 and 4,153,460. In the first case, such a fine, light insensitive emulsion has been used dispersed in a gelatin layer to absorb the development inhibiting compound released by such couplers. In the second case, the DIR compounds, together with 2-equivalent cyan forming couplers, have been combined with such a layer including a light insensitive, fine grain emulsion to increase the sensitivity of the red-sensitive layer.

A technique known to provide high-sensitivity photographic materials is the multilayer technique (described in GB patent 923,045) which consists of using more layers with different sensitivities (also called hemilayers) for the formation of at least one of the three main colors which form a conventional color image (cyan, magenta and yellow). The more sensitive, coarse grain emulsion is used to record low exposures and the less sensitive emulsion is used to record higher intensity exposures. Of course, the two emulsions, sensitive to the same region of light and forming the same color, are chosen in their sensitometric curves (which define sensitivity, contrast and maximum density), to match and form the desired sensitometric curve, as known in the art. In this sense, we can speak of "matched" hemilayers. The more sensitive emulsion is used in a higher quantity with respect to the less sensitive emulsion but contains a lower proportion of coupler (i.e. a high silver/coupler ratio). This is true also when three emulsions are used respectively to record low, middle and high exposures (as described in US patent 3,843,369). In any case, the lowest sensitivity emulsion is used in a lower quantity with respect to the highest sensitivity emulsion or emulsions, but with a relatively higher coupler quantity, i.e. with a low silver/coupler ratio. This attempts to provide a material having the sensitivity of the most sensitive layer and the grain characteristics of the least sensitive layer. Such techniques, however, have not sufficiently provided the man skilled in the art with means to improve sensitivity and quality as desired.

Summary Of The Invention

According to the present invention it has been found that the sensitometric characteristics of a photographic material can be improved as desired, if a layer packet is used which comprises in the indicated order starting from the base outwards, at least a red-sensitive layer including a cyan forming coupler, a layer including from 0.1 to 1 gram of silver per square meter of a fine grain light insensitive silver halide emulsion and at least a green-sensitive layer including a DIR compound associated with a magenta forming coupler. It has been found in particular that the beneficial effects of the presence of the light insensitive emulsion layer occurred not only in the green-sensitive layer where the DIR compound was present, but also in the red-sensitive layer where no DIR coupler was present.

Still in particular, it has been found that the multilayer technique, according to which the layers, in particular the magenta and/or cyan layer, each consist of two or more layers having different sensitivities, is particularly suitable to the purposes of the present invention.

Detailed Description Of The Invention

The present invention refers to a multilayer color photographic material comprising gelatin silver halide emulsion layers respectively sensitive to the red, to the green and to the blue regions of the light and respectively being capable of forming cyan, magenta and yellow images upon coupling with oxidized color developer. The green layer or layers include DIR compounds associated with magenta forming couplers and are coated on a light insensitive fine grain silver halide emulsion layer on its turn coated on said red sensitive layer or layers at a silver coverage of 0.1 to 1 gram per square meter, preferably of 0.2 to 0.4 gram per square meter.

Preferably, the present invention refers to a multilayer color photographic material as described above, wherein two green-sensitive hemilayers are used, respectively having a low and a high sensitivity, to form the magenta image and two red-sensitive hemilayers are used, respectively having a low and a high sensitivity, to form the cyan image.

More preferably, the present invention refers to a multilayer color photographic material as described above, wherein a third red-sensitive middle-sensitivity hemilayer is used in addition to said low and high sensitivity hemilayers.

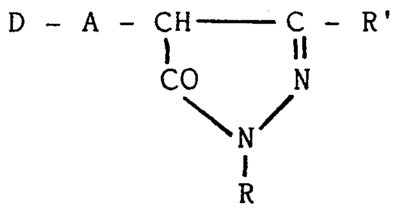
Still more preferably, the present invention refers to a multilayer color photographic material as described above which includes layers coated one on the other starting from the base, in the order: red-sensitive low-sensitivity layer, red-sensitive middle-sensitivity layer, red-sensitive high-sensitivity layer, non-sensitive layer, green-sensitive low-sensitivity layer, green-sensitive high-sensitivity layer, yellow filter layer, blue-sensitive low-sensitivity layer, blue-sensitive high-sensitivity layer.

In particular, the present invention refers to a multilayer color photographic material as described above, wherein said DIR compound is a DIR coupler represented by general formula (I):

$$\mathrm{COUP} - \mathrm{Z} \qquad \text{(I)}$$

wherein COUP represents a magenta coupler residue (such as e.g. a 5-pyrazolone coupler, a pyrazolobenzimidazole coupler, a cyanoacetylcumarone coupler and a indazolone coupler) which couples with the oxidation product of a developing agent of the primary aromatic amine type to give a magenta dye and Z represents an organic residue which can be released by (I) during the coupling reaction with the oxidation product of the primary aromatic amine to inhibit development in the silver halide emulsion layer (examples of such organic residue being heterocyclic residues which form 1-triazole or 1-diazole rings, 2-benzotriazole residues, arylmonothio groups and thioetherocyclic groups).

More in particular, the present invention refers to a multilayer color photographic material as described above wherein said DIR coupler is represented by general formula (II):



(II)

wherein R represents an aryl group, a heterocyclic group, an alkyl group; R' represents an alkyl group, an alkoxy group, an aryloxy group, an aryl group, a heterocyclic ring residue, an amino group, an arylamino group, a ureido group; A represents sulfur or selenium and D represents a group which, together with the sulfur or selenium of the thioether or selenoether bond, when such atom is released during coupling, forms a compound exerting a development inhibiting effect.

The present invention preferably refers to a multilayer color photographic material as described above wherein the non light-sensitive silver halide included in the intermediate layer is silver bromo-iodide, more preferably silver bromo-iodide containing from 1 to 4 per cent of silver iodide moles, and the most preferably silver bromo-iodide containing about 2 per cent of silver iodide moles.

More preferably the present invention refers to a multilayer color photographic material as described above wherein the light insensitive silver halide grains have mean sizes lower than 0.2 μ, more preferably lower than 0.1 μ.

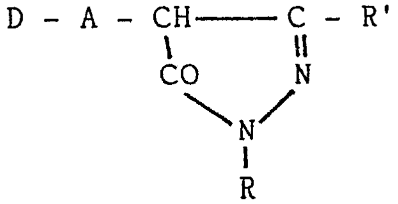
The DIR compounds used in the practice of the present invention are those compounds which during development release a development inhibiting compound. Compounds of this type are for instance the DIR couplers which release a development inhibiting compound during the reaction with the oxidation product of a color developer to form a dye, such as those described e.g. in US patent 3,227,554; the TIMING-DIR couplers which release a development inhibiting compound with the capability of controlling the release time, such as those described e.g. in GB patent applications 2,010,818 and 2,072,363; DIR hydroquinones which release a development inhibiting compound upon oxidation-reduction exchange with the oxidation products of the color developing agent, such as those described in US patents 3,639,417 and 3,379,529; other DIR substances which release development inhibiting compounds during the reaction with the oxidation product of a color developing agent to form a substantially colorless compound, such as those described in US patents 3,958,993; 3,961,959; 3,938,996; 3,928,041 and 3,632,345.

The DIR couplers, which are the DIR compounds preferred to the purposes of the present invention, can be represented by the following formula (I):

$$\text{COUP} - \text{Z} \qquad \text{(I)}$$

wherein COUP represents a magenta coupler residue which reacts with the oxidation products of a developing agent of the primary aromatic amine type to give a magenta dye and Z represents an organic group which can be released during coupling reaction and inhibits development. Examples of such couplers are the 5-pyrazolone couplers, the pyrazoloindazole couplers, the cyanoacetylcumarone couplers, the indazolone couplers. Examples of groups represented by Z are the heterocyclic residues which form 1-triazole and 1-diazole rings, the 2-benzotriazole residues, the arylmonothio and thioetherocyclic groups, such as those described in US patents 3,617,291; 3,622,328; 3,632,373; 3,620,745; 3,627,747; in GB patents 1,201,110; 1,261,061; 1,269,075 and 1,269,073. Other examples of such groups are described in US patents 3,818,570; 3,244,521; 3,499,761; 3,473,924; 3,575,699 and 3,554,757; in GB patents 919,061 and 1,031,262; in FR patents 1,346,227 and 1,594,983 and in DE patent 1,294,188.

Preferably, the DIR couplers of the present invention are those represented by the following formula (II):

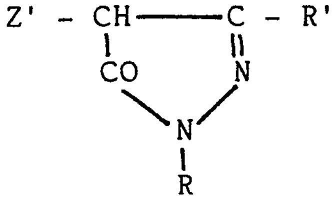


(II)

wherein R represents an aryl group (e.g. naphthyl, phenyl, 2,4,6-trichlorophenyl, 2-chloro-4,6-dimethylphenyl, 2,6-dichloro-4-methoxyphenyl, 4-methylphenyl, 4-acylaminophenyl, 4-alkylaminophenyl, 4-trifluoromethylphenyl, 3,5-dibromophenyl, etc.), a heterocyclic group (e.g. benzofuranylbenzothiazolyl, quinolyl, etc.) or a primary, secondary or tertiary alkyl group (e.g. methyl, ethyl, t-butyl, benzyl, etc.); R' represents a primary, secondary or tertiary alkyl group (e.g. methyl, propyl, n-butyl, tert.-butyl, hexyl, 2-hydroxyethyl, 2-phenylethyl, pentadecyl, etc.), an alkoxy group (e.g. methoxy, ethoxy, benzyloxy, etc.), an aryloxy group (e.g. phenoxy), an aryl group (e.g. phenyl, 2,4-ditert.-phenyl, etc.), a heterocyclic ring residue (e.g. quinolinyl, piperidyl, benzofuranyl, oxazolyl, etc.), an amino group (e.g. methylamino, diethylamino, phenylamino, tolylamino, 4-(3-sulfobenzamino)-anilino, 2-chloro-5-acylaminoanilino, 2-chloro-5-alkoxycarbonilanilino, etc.), an acylamino group (e.g. alkylcarbonamido such as ethylcarbonamido, etc., arylcarbonamido, heterocyclic carbonamido such as benzothiazolylcarbonamido, sulfonamido, heterocyclic sulfonamido, etc.), a ureido group (e.g. alkylureido, arylureido, heterocyclic ureido, etc.); A represents sulfur or selenium and D represents a group which, together with sulfur or selenium of the thioether or selenoether bond, forms a development inhibiting compound which can be released during the coupling reaction. Typical examples of D include an aryl group and a heterocyclic ring. Typical examples of said group, wherein D and sulfur or selenium are linked, include, if A is sulfur, a heterocyclic mercapto residue, e.g. a mercaptotetrazole (in particular 1-phenyl-5-mercaptotetrazole, 1-nitrophenyl-5-mercaptotetrazole, 1-naphthyl-5-mercaptotetrazole), a mercaptothiazole (in particular 2-mercaptobenzothiazole, mercaptonaphthothiazole), a mercaptooxadiazole, a mercaptopyrimidine, a mercaptooxazole, a mercaptothiadiazole, a mercaptotriazine and a mercaptotriazole and, as an arylmercapto group residue, include for instance a mercaptobenzene (in particular 1-mercapto-2-benzoic acid, 1-mercapto-2-nitrobenzene, 1-mercapto-3-heptadecanoylaminobenzene). If A is selenium, as the selenoheterocyclic group, 1-phenyl-5-selenotetrazole, 2-selenobenzoxazole are for instance included and, as the arylseleno group, a selenobenzene [e.g. 4-(4-hydrophenylsulfonyl)selenophenol] is for instance included. Concrete exemplification of the DIR coupler used in the present invention and the preparation thereof are for instance described in US patents 3,227,554 and 3,773,201.

In order to render the DIR couplers non diffusible, a group having a hydrophobic residue with about 8 to 32 carbon atoms is introduced into the coupler molecule. Such a residue is called "ballast group". The ballast group is linked to the coupler nucleus directly or through an imino, ether, carbonamido, sulfonamido, ureido, ester, imido, carbamoyl, sulfamoyl, etc. bond. Examples of ballast groups are specifically illustrated in US patent 4,009,038.

The magenta-dye forming couplers used in the green sensitive emulsion layer can be 5-pyrazolone couplers, pyrazolotriazole couplers, pyrazolobenzimidazole couplers, cyanoacetylcumarone couplers, indazolone couplers. In particular, the couplers represented by the following formula (III) are useful in this invention:



(III)

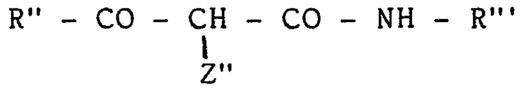
wherein R and R' have the above described meanings and Z' represents a hydrogen atom or a group which can be released during color development, such as a thiocyano group, an acyloxy group, an aryloxy group, an alkoxy group, an alkoxycarbonyloxy group, an amino group such as alkylamino, arylamino, alkylsulfonamido, arylsulfonamido, arylamido, cyclic imino, cyclic imido, etc., an arylazo group, an azoheterocyclic group, a heterocyclic group, as described for instance in GB patent 1,603,223 and in US patent 4,262,087. Such couplers are made non diffusible by means of ballasting groups as described above for the DIR couplers.

The green-sensitive silver halide emulsion layer for the purposes of the present invention, preferably consists of two or more emulsion hemilayers with different sensitivities. These green-sensitive hemilayers can be used in combinations of different silver/coupler ratios and of different color maximum densities. In particular, to the purpose of a batter utility, it has been found that the sensitivity difference between the higher sensitivity layer and the lower sensitivity layer is usefully in the range from 3 to 8 DIN, more preferably from 4 to 6 DIN (the sensitivity in the DIN system is derived from the exposure required to produce a density of 0.1 above fog in the curve of density vs. $\log_{10}$ of exposure, as described in P. Glafkidès, Chimie Photographique, 1957, p. 196, Publ. P. Montel, Paris); that the silver/coupler mole ratio of the more sensitive layer is in the range from 30/1 to 100/1, more preferably from 50/1 to 80/1 and the silver/coupler mole ratio of the less sensitive layer is in the range from 5/1 to 20/1, more preferably from 10/1 to 15/1 and that the difference of color maximum density between the lower sensitivity layer and the higher sensitivity layer is in the optical density value range of 0.3 to 0.9, more preferably 0.4 to 0.8. The DIR compounds and the magenta-dye forming couplers can be included in the same green-sensitive silver halide emulsion layer or by separate hemilayers. Preferably, each of these hemilayers, if any, contains the DIR compound in combination with the magenta forming coupler and at least one, and preferably all of them also contain the so-called masked magenta coupler, i.e. a colored coupler corresponding to the above formula (III), wherein Z' represents an arylazo group or an azoheterocyclic group.

The total quantity of magenta forming coupler contained in the green-sensitive silver halide emulsion layer or layers is in general in the range from 10 to 50 moles, more preferably from 20 to 40 moles per silver mole and the quantity of DIR coupler included in the layer is in general in the range from 2 to 10 moles, more preferably from 4 to 8 moles per silver halide mole; said DIR coupler is used in combination with the magenta-dye forming coupler in a quantity ranging from 5 to 40 mole per cent, preferably from 10 to 30 mole per cent with respect to the total moles of magenta-dye forming coupler in the green-sensitive layer.

Usefully, said DIR couplers and magenta-dye forming couplers can be included into one or more silver halide emulsion layers which build up the green-sensitive silver halide emulsion layer by various methods known in the photographic art. Couplers having a water-soluble group, such as a carboxyl group, a hydroxy group, a sulfonic group or a sulfonamido group, can be added to the emulsion according to the Fisher process, i.e. by dissolving them in an alkaline water solution. Hydrophobic couplers can be added to the silver halide emulsion by dissolving them in a high-boiling solvent and then dispersing them in gelatin as described in US patents 2,322,027 and 2,304,939. Alternatively, it is possible to add at least one coupler according to the Fisher process and the others according to the dispersion method.

The blue-sensitive silver halide emulsion layer of the photographic material contains at least a yellow-dye forming coupler of the acylacetanilido type. Particularly useful in this invention are the couplers represented by general formula (IV):

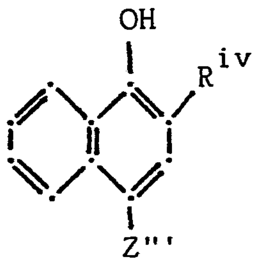


$$R'' - CO - \underset{\displaystyle Z''}{\underset{|}{CH}} - CO - NH - R''' \qquad (IV)$$

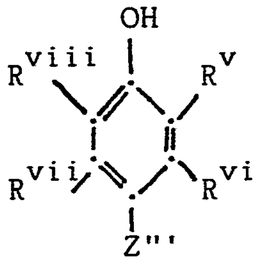
wherein R" represents a primary, secondary or tertiary alkyl group (e.g. tert.-butyl, 1,1-dimethylpropyl, 1,1-dimethyl-1-methoxy-fenoxymethyl, etc.), or an aryl group (e.g. phenyl, alkylphenyl such as 2-methylphenyl, 3-octadecylphenyl, etc. and alkoxyphenyl such as 2-methoxyphenyl, 4-methoxyphenyl, etc., halophenyl, 2-chloro-5-alkylcarbonamidophenyl, 2-chloro-5-[α-(2,4-ditert.-aminophenoxy)-butyramido]-phenyl, 2-methoxy-5-alkylamidophenyl, 2-chloro-5-sulfonamidophenyl, etc.); R''' represents a phenyl group (e.g. 2-chlorophenyl, 2-halo-5-alkylamidophenyl, 2-chloro-5-[α-(2,4-ditert.-amylphenoxy)-acetamido]-phenyl, 2-chloro--5-(4-methylphenylsulfonamido)-phenyl, 2-methoxy-5-(2,4-ditert.-amylphenoxy)-acetamidophenyl, etc.) and Z" represents a hydrogen or a group which can be released during color development, such as a halogen atom (in particular fluorine), an acyloxy group, an aryloxy group, an aromatic heterocyclic carbonyloxy group, a sulfimido group, an alkylsulfoxy group, an arylsulfoxy group, a phthalimido group, a dioxyimidazolidinyl group, a dioxyoxazolidinyl group, a dioxythiazolidinyl group, a dioxymorpholino group, etc., as described e.g. in US patents 3,227,550; 3,253,924; 3,277,155; 3,265,506; 3,408,194 and 3,415,652; in FR patent 1,411,384; in GB patents 944,490; 1,040,710 and 1,118,023; in DE-OS

2,057,941; 2,163,812; and 2,219,917 and in US patent application S.N. 469,923 filed on May 14, 1974.

The red-sensitive silver halide emulsion layer of the photographic element contains at least a cyan-dye forming coupler of the napthole or phenole type. In particular, couplers useful in this invention are those represented by general formulas (V) and (VI):



(V) and



(VI)

wherein R^{iv} represents a substituent used for cyan couplers, such as a carbamyl (e.g. alkylcarbamyl, arylcarbamyl, such as phenylcarbamyl, etc., a heterocyclic carbamyl, such as benzylthiazolylcarbamyl, etc.), a sulfamyl (e.g. alkylsulfamyl, arylsulfamyl such as phenylsulfamyl, etc., a heterocyclic sulfamyl, etc.), an alkoxycarbonyl, an aryloxycarbonyl, etc. R^{v} represents an alkyl group, an aryl group, a heterocyclic group, an amino group (e.g. alkylcarbonamido, arylcarbonamido, etc.), a sulfamido group, a sulfamyl group or a carbamyl group; R^{vi}, R^{vii} and R^{viii} each have the same meaning of R^{iv} and moreover represent a halogen atom or an alkyl group and Z''' represents a hydrogen atom or a group which can be released during color development, such as a halogen atom, a thiocyano group, a cycloimido group (e.g. maleido, sucinimido, 1,2-dicarboxyimido, etc.), an arylazo group or a heterocyclic azo group.

Such yellow-dye and cyan-dye forming couplers are made non diffusible by means of ballast groups and are introduced into one or more emulsion layers, as described above.

The red-sensitive and blue-sensitive silver halide emulsion layers can contain the DIR compounds (such as DIR couplers, TIMING-DIR couplers, DIR hydroquinones or other DIR substances) as said above in association with the cyan and yellow dye forming couplers. Normally, the use of such DIR compounds in these layers does not show significant advantages, but may sometimes be advisable to achieve particular results.

The intermediate layer coated between the red-sensitive silver halide emulsion layers and the green-sensitive emulsion layers contains fine, light insensitive silver halide grains (light insensitive grains herein mean those grains which upon exposure at the normal employment conditions and development in standard black and white and color developers do not form any image). Such silver halide grains are neither physically ripened nor chemically sensitized and have a mean size lower than about 0.2 μ, more preferably lower than 0.1 μ. The useful silver halide can be one among silver chloride, silver bromide, silver iodide, silver bromo-iodide, silver chloro-bromide, silver chloro-bromo-iodide, etc., used alone or in combination of two or more of them. In the practice of the present invention, silver bromo-iodide having no more than 4% silver iodide moles proved to be very effective in providing the beneficial effects in the green-sensitive silver halide emulsion layer (or layers). Since these silver halide crystals are not to be light sensitive, they must not get bigger during preparation, storage and coating and after the coating itself of the photographic material containing them. In this respect, silver bromo-iodide crystals having from 1 to 4% silver iodide moles were particularly good, in particular when stabilized during the preparation thereof, preferably with triazoindolizine compounds.

It is believed that, for the purposes of the present invention, said fine, light insensitive silver halide crystals have to be a little soluble in the developing solutions to give a contribution to the silver image formation. In fact a part of the image is formed upon chemical development, i.e. upon reduction of the exposed silver halide grains, and a part is formed upon physical development, i.e. upon passage into solution of silver ions from developing or neighbouring grains, then diffusion of such ions to the silver centers (such as those supplied by the latent image or by the chemical development) where they are reduced to silver. The fine light insensitive silver halide grains of the present invention are supposed to act as a source of silver ions which diffuse into adjacent light-sensitive layers to contribute to the silver image formation upon physical development.

The amount of such light insensitive silver halide grains useful to obtain the desired effects in the adjacent light-sensitive layers is in the range of about from 0.1 to 1 gram per square meter, preferably from about 0.2 to 0.4 gram per square meter.

Very useful effects using the present invention were seen in the green-sensitive silver halide emulsion layer, wherein the DIR couplers are used to improve definition, in particular in the green-sensitive silver halide emulsion layers used for high-sensitivity multilayer color photographic materials. Since the development inhibiting substances released by the DIR compounds during development decrease sensitivity and developability of the light-sensitive material the use thereof is limited and it was found to be difficult to increase image definition in the magenta layer without causing negative adverse affects to other photographic properties. The presence of such light insensitive fine silver halide grains in the above quantities led to an increase in sensitivity and developability (this latter being evidenced by a higher maximum color density of the image) in said green-sensitive silver halide emulsion layer. Beneficial effects were evidenced also in the adjacent red-sensitive silver halide emulsion layer which showed an increase of both its sensitivity and maximum density values.

Higher maximum density and sensitivity characteristics obtained according to the present invention can be spent in reducing the silver coverage in the green-sensitive and red-sensitive silver halide emulsion layers and, consequenlty, in reducing the thickness of said layers and increasing the image quality of the photographic material. Quantities of light insensitive silver halide lower than 0.1 gram per square meter did not show the beneficial effects of the present invention and quantities higher than 1 gram per square meter led to a decrease of the image quality.

The intermediate layer, comprising the light insensitive silver halide grains of the present invention, can at the same time include other compounds of photographic interest, such as matting agents (e.g. colloidal silica, polymethylmethacrylate, etc.), high-boiling solvents (e.g. tricresylphosphate, dibutylphthalate, etc.), UV-absorbers (e.g. thiazolidone, benzothiazole, acrylonitrile, benzophenone compounds, etc.), antioxidants, ballasted hydroquinone derivatives, surfactants such as coating aids, gelatin hardeners, etc. As a binder for the light insensitive particles, gelatin is used in general, but instead of a part or of whole the gelatin, colloidal albumin, agar, arabic gum, alginic acid, cellulose derivatives such as hydrolized cellulose acetate, carboxymethylcellulose, hydroxyethylcellulose, etc., as well as synthetic binders, for instance polyvinyl alcohol, partially saponified polyvinyl acetate, polyacrylamide, poly-N,N-dimethylacrylamide, poly-N-vinylpyrrolidone, water-soluble polymers, as described in US patents 3,847,620; 3,655,389; 3,341,332; 3,615,424 and 3,860,428, gelatin derivatives, for instance acylated gelatin, phenylcarbamylated gelatin, phthalated gelatin, as described in US patents 2,614,928 and 2,525,753 and a graft polymerization product obtained from a monomer having a polymerizable ethylene group such as acrylic acid (or ester), methacrylic acid (or ester) and acrylonitrile, as described in US patents 2,548,520 and 2,831,767 and gelatin can be used.

The silver halide emulsions used in the red-sensitive, green-sensitive and yellow-sensitive layers of the present invention are a fine dispersion of silver chloride, silver bromide, silver chloro-bromide, silver iodo-bromide, silver chloro-iodo-bromide in a hydrophilic polymer. As a hydrophilic polymer, the conventional polymers used in the photographic art can be advantageously used. They include gelatin, a gelatin derivative such as acylated gelatin, graft gelatin, etc., albumin, arabic gum, agar agar, a cellulose derivative such as hydroxyethylcellulose, carboxymethylcellulose, etc., a synthetic resin such as polyvinyl alcohol, polyvinylpyrrolidone, polyacrylamide, etc. The silver halide can have uniform grain sizes or a broader distribution of the grain sizes. Furthermore, the silver halide grain sizes range from about 0.1 µ to about 3 µ. The silver halide emulsion can be prepared by following a single-jet, double-jet method or a combination of such methods or can be ripened using for instance an ammonia, a neutralization or an acid method, etc.

The silver halide emulsion used as the light-sensitive emulsion layer in this invention can be chemically sensitized such as, for instance, by a gold sensitization method as described in US patents 2,399,083; 3,597,856 and 2,597,915; a reduction sensitization method as described in US patents 2,487,850 and 2,521,925; a sulfur sensitization method as described in US patents 1,623,499 and 2,410,689; a sensitization method using metal ions other than silver as described in US patents 2,566,263; 2,566,245 and 2,566,263; or a combination of these methods.

The silver halide emulsion can be also sensitized using a spectral sensitization method which is generally employed in producing color photographic materials. For such purpose, a sensitizing dye, such as a cyanine dye or a merocyanine dye, as described in US patents 2,526,632; 2,503,776; 2,493,748; 3,384,486; 2,933,390 and 2,933,089 can be suitably used. The silver halide emulsion used in this invention can further contain a stabilizer such as a 4-hydroxy-1,3,3a,7-tetrazaindene derivative, etc., an antifoggant such as a mercapto compound and a benzotriazole derivative, a coating aid, a hardening agent, a wetting agent, a sensitizer such as an onium derivative, for instance a quaternary ammonium salt as described in US patents 2,271,623 and 2,288,226 and also a polyalkylene oxide derivative as described in US patents 2,708,162; 2,531,832; 2,533,990; 3,210,191 and 3,158,484. The silver halide emulsion layer further can contain an irradiation preventing dye.

Furthermore, the color photographic material of this invention can contain layers such as a filter layer, a mordant dye-containing layer, a colored layer containing a hydrophobic dye, etc.

The silver halide emulsions used in this invention can be coated on various supports such as, for instance, a cellulose acetate film, a polyethylene terephthalate film, a polyethylene film, a polypropylene film, a glass plate, a baryta-coated paper, a resin- coated paper or a synthetic paper.

The photographic material of this invention is processed with a color developer containing,as a color developing agent, a primary aromatic amine compound such as a p-phenylene diamine derivative and a p-aminophenol compound. Examples of preferred p-phenylene diamine derivatives are p-amino-N- ethyl-N-ß-(methanesulfonamidoethyl)-m-toluidine sesquisulfate monohydrate, diethylamino-p-phenylene diamine sesquisulfate, p-amino-N,N-diethyl-m-toluidine hydrochloride, p-amino-N-ethyl-N-ß-hydroxyethyl-aniline sesquisulfate monohydrate, and the like.

The color photographic materials of this invention can be developed using developers generally used for developing conventional color photographic negative materials, cine color photographic negative or positive materials, color photographic papers, and instant color photographic materials. For instance, the color development processes as described in the specification of GB patent 1,203,316; in US patent 3,695,883; in US patent application S.N. 234,163, filed on Mar. 13, 1972 and S.N. 240,287, filed on Mar. 31, 1972; in H. Gordon, The British Journal Of Photography, page 559 et seq., Nov. 15, 1954; ibid., page 440 et seq., Sept. 9, 1955; and ibid., page 2 et seq., Jan. 6, 1956; in S. Horwitz, The British Journal Of Photography, page 212 et seq., Apr. 22, 1960; in E. Gehret, The British Journal Of Photography, page 122 et seq., Mar. 4, 1960 and ibid, page 396 et seq., May 7, 1965; J. Meech, The British Journal Of Photography, page 182 et seq., Apr. 3, 1959; and in the specification of German Offenlegungsschrift (OLS) 2,238,051, can be used.

Example 1

A multilayer color photographic film (Film A) was prepared by coating on a cellulose triacetate base subbed with gelatin and cellulose diacetate the following layers in the indicated order:

first layer: a low red sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a red sensitized silver chloro-bromo-iodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles blended with a red sensitized silver bromo-iodide gelatin emulsion containing 2% silver iodide moles) having a dry thickness of 2.5 μ, containing 1.2 g/m^2 of silver and the couplers 1-hydroxy-4-{4-[(N-ethyl-N-(3,5-dicarboxymethylphenyl)-amino)-sulfonyl]- phenylazo}-N-[2-methyl-5-(1-oxododecyl)-phenyl]-

2-naphthalencarboxamide (Coupler A) and 1-hydroxy-N-[δ-(2,4-ditert.amylphenoxy)-n-butyl]-naphthamide (Coupler B), dispersed together in a mixture of tricresylphosphate and dibutylphthalate, at a total coupler coverage of 0.95 g/m^2;

<u>second layer:</u> high red sensitivity silver bromo-iodide emulsion layer (consisting of a red sensitized silver bromo-iodide gelatin emulsion having 7% silver iodide moles) having a dry thickness of 0.8 μ, containing 0.6 g/m^2 of silver and the couplers A and 1-hydroxy-2,4-dichloro-3-methyl-6-{α-(3-pentadecylphenoxybutyramido)}-phenol (Coupler C), dispersed in tricresylphosphate, at a total coupler coverage of 0.035 g/m^2;

<u>third layer:</u> intermediate layer containing 1.6 g/m^2 of gelatin and 0.20 g/m^2 of 2,5-diisoctylhydroquinone dispersed in tricresylphosphate;

<u>fourth layer:</u> low green sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a green sensitized blending of the two silver halide gelatin emulsions of the first layer) having a dry thickness of 2.6 μ, containing 1.9 g/m^2 of silver and the couplers 1-(2,4,6-trichlorophenyl)-3- {3-[α-(2,4-ditert.amylphenoxy)-acetamido]-benzamido}-4-(p-methoxyphenylazo)-5-pyrazolone (Coupler D), 1- (2,4,6-trichlorophenyl)-3-{3-[α-(2,4-ditert.amylphenoxy)-acetamido]-benzamido}-5-pyrazolone (Coupler E) and 1-{4-[α-(2,4-ditert.amylphenoxy)-acetamido]-phenyl}-3-ethoxy-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone (Coupler F), dispersed in tricresylphosphate, at a total coupler coverage of 0.9 g/m^2;

<u>fifth layer:</u> high green sensitivity silver bromo-iodide emulsion layer (consisting of a green sensitized silver bromo-iodide emulsion having 7% silver iodide moles) having a dry thickness of 1.2 μ, containing 1.3 g/m^2 of silver and the couplers D, E and F, dispersed in tricresylphosphate, at a total coupler coverage of 0.1 g/m^2;

<u>sixth layer:</u> yellow filter layer, containing 0.05 g/m^2 of yellow

colloidal silver and 0.07 g/m^2 of 2,5-diisoctylhydroquinone, dispersed in tricresylphosphate, and having a thickness of 1.2 μ.

A second, third and fourth color photographic films (Films B, C and D) were prepared similarly to film (A) with the only difference that the third layer had the following composition: intermediate layer containing 1.6 g/m^2 of gelatin and 0.25 g/m^2 of the light insensitive silver bromo-iodide emulsion having 2% silver iodide moles and a mean grain size of 0.1 μ (Film B), 0.6 g/m^2 of gelatin and 0.1 g/m^2 of the above light insensitive silver bromo-iodide emulsion (Film C), 2,6 g/m^2 of gelatin and 0.5 g/m^2 of the above light insensitive silver bromo-iodide emulsion (Film D), all films containing 0.20 g/m^2 of 2,5-diisoctylhydroquinone dispersed in tricresylphosphate.

A fifth color photographic film (Film E) was prepared by coating on a subbed cellulose triacetate base the following layers in the indicated order:

first layer: the same first low red sensitivity layer of Film A;

second layer: the same second high red sensitivity layer of Film A;

third layer: the same intermediate layer of Film B;

fourth layer: the same low green sensitivity layer of Film A, but having the coupler 1-{4-[α-(2,4-ditert.amylphenoxy)-butyramido]-phenyl} -3-(1-pyrrolidino)-4-(1-phenyl-5-tetrazolylthio)-5-pyrazolone (Coupler G), instead of Coupler F;

fifth layer: the same high green sensitivity layer of Film A, but having Coupler G instead of Coupler F;

sixth layer: the same yellow filter layer of Film A.

A sixth color photographic film (Film F) was prepared by coating on a subbed cellulose triacetate base the following layers in the indicated order:

first layer: low red sensitivity silver chloro-bromo-iodide emulsion layer (consisting of the same red sensitized blending of two silver halide gelatin emulsions of the first layer of Film A) having a dry thickness of 2.2 μ, containing 1.05 g/m^2 of silver and 0.85 g/m^2 of the couplers of Film A;

<u>second layer:</u> the same high red sensitivity layer of Film A;

<u>third layer:</u> the same intermediate layer of Film B;

<u>fourth layer:</u> low green sensitivity chloro-bromo-iodide emulsion layer (consisting of the same green sensitized blending of two silver halide gelatin emulsions of the fourth layer of Film A) having a dry thickness of 2.3 μ, containing 1.7 g/m^2 of silver and 0.8 g/m^2 of the couplers of Film A;

<u>fifth layer:</u> the same high green sensitivity layer of Film A;

<u>sixth layer:</u> the same yellow filter layer of Film A.

Samples of the above films were exposed at 5500°K under a continuous wedge and processed in a Kodak C41 developer at 38°C. The results are reported in the following table:

Film	Maximum density		Speed*	
	cyan	magenta	cyan	magenta
A	2.34	2.52	20.8	22.4
B	2.87	2.89	21.7	23.1
C	2.62	2.72	21.3	22.9
D	2.75	2.89	21.8	22.7
E	2.88	2.83	21.7	22.7
F	2.78	2.75	21.6	23.0

*) expressed in DIN values.

The data above show that the constructions of the present invention (Films B to F) consistently show an improved maximum density and increased speed over a construction (Film A) without the light insensitive superfine silver halide grains of the present invention.

Example 2

A multilayer color photographic film (Film A) was prepared by coating on a subbed cellulose triacetate base the following layers in the indicated order:

first layer: antihalo layer containing gelatin in a quantity of 4 g/m^2 and colloidal black silver in a quantity of 0.2 g/m^2;

second layer: low red sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a red sensitized silver chloro-bromo--iodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles) having a dry thickness of 3 μ, containing 1.4 g/m^2 of silver and the couplers A and B of example 1, dispersed in tricresylphosphate, at a total coupler coverage of 0.44 g/m^2;

third layer: high red sensitivity silver bromo-iodide emulsion layer (consisting of a silver bromo-iodide gelatin emulsion containing 7.2% silver iodide moles) having a dry thickness of 1.9 μ, containing 1.8 g/m^2 of silver and the couplers C and B of example 1, dispersed in tricresylphosphate, at a total coupler coverage of 0.12 g/m^2;

fourth layer: intermediate layer containing 1.58 g/m^2 of gelatin and 0.24 g/m^2 of 2,5-diisoctylhydroquinone dispersed in tricresylphosphate;

fifth layer: low green sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a green sensitized silver chloro-bromo-iodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles) having a dry thickness of 3.2 μ, containing 1.6 g/m^2 of silver and the couplers D, E and F of example 1 at a total coupler coverage of 0.39 g/m^2;

sixth layer: high green sensitivity silver bromo-iodide emulsion layer (consisting of a green sensitized silver bromo-iodide gelatin emulsion containing 7.2% silver iodide moles) having a dry thickness of 2.3 μ, containing 2 g/m^2 of silver and the couplers 1-(2,4,6-trichlorophenyl)-3-(p-dodecylphenylcarbamoylamino)-5-pyrazolone and F at a total coupler coverage of 0.20 g/m^2;

seventh layer: yellow filter layer, containing 0.95 g/m^2 of gelatin, yellow colloidal silver and 2,5-diisoctylhydroquinone dispersed in tricresylphosphate, having a thickness of 1.1 μ;

eighth layer: low blue sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a blend of a low sensitivity silver chloro-bromo-iodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles and a still lower sensitivity silver bromo-iodide gelatin emulsion containing 2% silver iodide moles) having a dry thickness of 3.7 μ, containing 0.75 g/m^2 of silver and the coupler α-pivaloyl-α-(3-chloro-1,2,4-triazolyl)-2-chloro-5-{α-(2,5-ditert.amylphenoxy)-propionamido}-acetanilide (Coupler H), dispersed in tricresylphosphate and diethyllauramide, at a coverage of 1.5 g/m^2;

ninth layer: high blue sensitivity silver bromo-iodide emulsion layer (consisting of a silver bromo-iodide gelatin emulsion containing 7.2% silver iodide moles) having a dry thickness of 2.3 μ, containing 0.9 g/m^2 of silver and the coupler H at a coverage of 0.37 g/m^2;

tenth layer: intermediate layer of 1.4 g/m^2 gelatin having a dry thickness of 1.2 μ and containing 2-(2'-hydroxy-3',5'-ditert.-butylphenyl)-5-tert.butyl-benzotriazole dispersed in tricresylphosphate and dibutylphthalate at a coverage of 0.23 g/m^2;

eleventh layer: top-coat protective layer of 0.8 g/m^2 gelatin having a dry thickness of 1 μ and containing polymethylmethacrylate particles at a mean size of about 3 μ.

A second and a third color photographic films (Films B and C) were prepared similarly to film (A) with the only difference that the fourth layer thereof had the following composition:

intermediate layer of 1.58 g/m^2 gelatin containing 2,5-diisoctylhydroquinone dispersed in tricresylphosphate and the above light insensitive silver bromo-iodide emulsion (having 2% silver iodide moles and a mean grain size of 0.1 µ) at a silver coverage respectively of 0.18 (Film B) and 0.36 (Film C) g/m^2.

Samples of the above films were exposed at 5500°K through a continuous wedge and developed in a Kodak C41 process at 38°C. The results are reported in the following table:

Film	Maximum density		Speed*	
	cyan	magenta	cyan	magenta
A	1.84	2.09	21.9	23.1
B	2.06	2.30	22.9	23.9
C	2.10	2.30	23.1	23.8

*) expressed in DIN values.

Sharpness (MTF) and granularity (RMS) of the image were tendentially better with Films B and C.

Example 3

A multilayer color photographic film (Film A) was prepared by coating on a polyethyleneterephthalate base, subbed with a first methylacrylate-itaconic acid-vinylidene chloride copolymer containing layer and with a second gelatin containing layer, the following layers in the indicated order:

first layer: antihalo layer containing 4 g/m^2 of gelatin and 0.2 g/m^2 of black colloidal silver;

second layer: low red sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a blend of a low sensitivity silver chloro-bromoiodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles and a still lower sensitivity silver bromo-iodide gelatin emulsion having 2% silver iodide moles) having a dry thickness of 2.9 µ, containing 1 g/m^2 of silver and the couplers A and B, dispersed in tricresylphosphate at a total coupler coverage of 0.81 g/m^2;

third layer: medium red sensitivity silver bromo-iodide emulsion layer (consisting of a red sensitized silver bromo-iodide gelatin emulsion containing 7% silver iodide moles) having a dry thickness of 1.2 μ, containing 0.8 g/m^2 of silver and the couplers A and C, dispersed in tricresylphosphate, at a total coupler coverage of 0.05 g/m^2;

fourth layer: high red sensitivity silver bromo-iodide emulsion layer (consisting of a red sensitized silver bromo-iodide gelatin emulsion containing 7% silver iodide moles) having a dry thickness of 2.9 μ, containing 2.6 g/m^2 of silver and the couplers C and B, dispersed in tricresylphosphate at a total coupler coverage of 0.87 g/m^2;

fifth layer: intermediate layer containing 1.16 g/m^2 of gelatin and 0.14 g/m^2 of 2,5-diisoctylhydroquinone dispersed in tricresylphosphate;

sixth layer: low green sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a blend of a low sensitivity chloro-bromo-iodide gelatin emulsion containing 5% silver chloride moles and 7% silver iodide moles and a still lower sensitivity silver bromo-iodide gelatin emulsion containing 2% silver iodide moles) having a dry thickness of 3.3 μ containing 1.2 g/m^2 of silver and the couplers D, E and F, dispersed in tricresylphosphate at a total coupler coverage of 0.6 g/m^2;

seventh layer: high green sensitivity silver bromo-iodide emulsion layer (consisting of a silver bromo-iodide green sensitized gelatin emulsion containing 7% silver iodide moles) having a dry thickness of 2.7 μ, containing 2.2 g/m^2 of silver and the couplers of the sixth layer at a total coupler coverage of 0.2 g/m^2;

eighth layer: yellow filter layer, containing 0.05 g/m^2 of gelatin, yellow colloidal silver and 0.05 g/m^2 of 2,5-diisoctylhydroquinone dispersed in tricresylphosphate;

ninth layer: low blue sensitivity silver chloro-bromo-iodide emulsion layer (consisting of a blend of a low sensitivity silver chloro-bromoiodide gelatin emulsion having 5% silver chloride moles and 7% silver iodide moles and a still lower sensitivity silver bromo-iodide emulsion having 2% silver iodide moles) having a dry thickness of 3.7 μ, containing 0.75 g/m^2 of silver and the coupler H, dispersed in tricresylphosphate at a coverage of 1.5 g/m^2;

tenth layer: high blue sensitivity silver bromo-iodide emulsion layer (consisting of a silver bromo-iodide gelatin emulsion containing 7.2% silver iodide moles) having a dry thickness of 2.3 μ, containing 0.9 g/m^2 of silver and the coupler of the ninth layer at a coverage of 0.37 g/m^2;

eleventh layer: protective layer of 0.94 g/m^2 of gelatin having a dry thickness of 1.2 μ and containing polymethylmethacrylate particles and a dispersion of 2-(2'-hydroxy-3',5'-ditert.butylphenyl)-tert.butyl-benzotriazole in a mixture of tricresylphosphate and dibutylphthalate.

A second multilayer color photographic film (Film B) was prepared similarly to film (A) with the only difference that the fifth intermediate layer had the following composition: layer of 1.2 g/m^2 of gelatin containing 0.14 g/m^2 of diisoctylhydroquinone dispersed in tricresylphosphate and the above light insensitive silver bromo-iodide emulsion (i.e. having 2% silver iodide moles and a medium grain size of 0.1 μ) at a silver coverage of 0.25 g/m^2.

Samples of films A and B were exposed at 5500°K through a K3 continuous wedge and developed in a Kodak C41 process at 38°C. The following table reports the sensitometric results and the MTF values:

Film	Maximum density		Speed*		MTF (visual)	
	cyan	magenta	cyan	magenta	at 10 l/mm	at 30 l/mm
A	2.12	2.43	21.1	22.1	88%	33%
B	2.35	2.70	22.1	22.7	95%	45%

*) expressed in DIN values.

Claims:

1. A multilayer color photographic material comprising at least three gelatin silver halide emulsion layers respectively sensitive to the red, to the green and to the blue regions of the light, and respectively capable of forming cyan, magenta and yellow images upon reaction with oxidized aromatic primary amine color developers, at least one green sensitive layer of which includes DIR compounds associated with magenta forming couplers, characterized by the fact that said at least one green sensitive DIR compound containing layer is coated on a light insensitive fine grain silver halide emulsion layer which is coated on at least one red sensitive layer at a silver coverage of 0.1 to 1 gram per square meter.

2. Photographic material according to claim 1, characterized by the fact that said at least one green-sensitive layer and said at least one red-sensitive layer reactively associated with said light insensitive layer each comprise two matched low and high sensitivity hemilayers respectively sensitive to the green and red region of the light.

3. Photographic material according to claim 2, characterized by including a third matched medium-sensitivity red-sensitive hemilayer.

4. Photographic material according to claim 3, characterized by the fact that it contains layers coated one with respect to the other starting from the base in the sequence low-sensitivity red-sensitive layer, medium-sensitivity red-sensitive layer, high-sensitivity red-sensitive layer, light insensitive layer, low-sensitivity green-sensitive layer, high-sensitivity

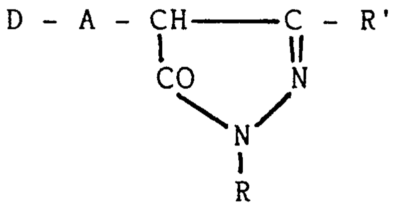
green-sensitive layer, yellow filter layer, low-sensitivity blue-sensitive layer, high-sensitivity blue-sensitive layer.

5. Color photographic material as claimed in claim 1, wherein said DIR compound is represented by general formula (I):

$$\text{COUP} - \text{Z} \qquad \text{(I)}$$

wherein COUP represents a magenta coupler residue which couples with the oxidation product of a developing agent of the primary aromatic amine type to give a magenta dye and Z represents an organic residue which is released by the coupler during the coupling reaction with the oxidation product of the developing agent of the primary aromatic amine type to inhibit development in the silver halide emulsion layer.

6. Color photographic material as claimed in claim 1, wherein said DIR compound is represented by general formula (II):



(II)

wherein R represents an aryl group, a heterocyclic group, an alkyl group; R' represents an alkyl group, an alkoxy group, an aryloxy group, an aryl group, a heterocyclic ring residue, an amino group, an acylamino group or a ureido group; A represents sulfur or selenium and D represents a group which, together with the sulfur or selenium of the thioether or selenoether bond, forms a development inhibiting compound which is released during the reaction with the oxidation product of the developing agent of the primary aromatic amine type.

7. Color photographic material, as claimed in claim 1, wherein said light unsensitive silver halide emulsion, which is included in the intermediate layer, is a silver bromo-iodide emulsion.

8. Color photographic material as claimed in claim 1, wherein said light insensitive silver halide emulsion, which is included in the intermediate layer, is a silver bromo-iodide emulsion containing 1 to 4 per cent silver iodide moles.

9. Color photographic material as claimed in claim 1, wherein said silver halide, which is included in the intermediate layer, has a mean grain size lower than 0.2 micron.