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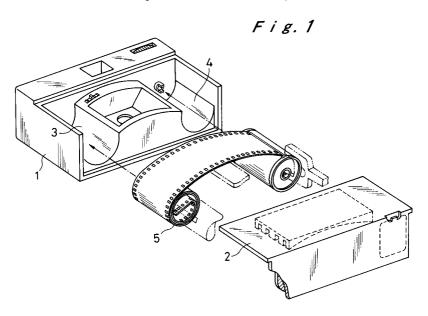
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⁵⁴ Photographic products.

There is disclosed a photographic product provided with an exposure function and preloaded with a photographic material, in which said photographic material comprises at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer, has a specific photographic sensitivity of 640 or more, contains 3.0 to 8.0 g/m² of silver in total content, and contains a palladium compound in an amount of 0.1 mg/m² or more in terms of palladium.



FIELD OF THE INVENTION

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The present invention relates to photographic products having been preloaded with a photographic material and having an exposure function, e.g., lens-equipped films (hereinafter referred to as film with a lens), and more particularly photographic products having been preloaded with a photographic material and having an exposure function, in which the color photographic material has a high sensitivity.

BACKGROUND OF THE INVENTION

Conventionally, products of so-called film with a lens are sold in two types: one type for outdoor photographing, used mainly under fine weather or light cloudy weather, and the other for indoor photographing for a short-distance object using a built-in strobe (electronic flash). As described, for example, in JP-B ("JP-B" means examined Japanese patent publication) No. 32615/1990, Publication of examined Japanese Utility Model Application No. 39784/1991, and Japanese Utility Model Application Nos. 75091/1986, 75794/1986, 126942/1986, 136276/1986, 139993/1986, 246977/1986, and 246978/1986, conventional photographic products having been preloaded with a photographic material and having an exposure function are photographic products wherein the photographic material is packed in a cartridge that is in conformity with the film size and is loaded in a packaged case having a lens, a shutter, a finder, a flash, and other functions.

Many of the optical systems used therein employ a fixed-focus lens having an F-number of 8 or over; many of them are designed such that the shutter mechanism has a fixed shutter speed of about 1/100 seconds and the film surface is placed in an imaging plane that is in a fixed position; and in many cases a color negative photographic material rated ISO 400 is preloaded.

In the case of a film with a lens for outdoor photographing, if the film is used in fine weather or light cloudy weather, satisfactory system sensitivity is obtained, whereas if the film is used in the evening or in rainy weather or is used for a shaded object or a back-lighted object even under bright conditions, the system sensitivity is unsatisfactory and the film becomes under-exposure, leading to a defect that a satisfactorily finished photograph cannot be obtained.

In the case of film with a lens having a builtin strobe for indoor photographing, many of them use a small strobe with a guide number of 10 or below and a fixed-focus lens having an F-number of 8 or over and are designed such that the film surface is placed in an imaging plane that is in a fixed position, and a color negative photographic material rated ISO 400 is preloaded. If they are used for an object that is within 3 meters from the film, the system sensitivity is satisfactory, whereas if the distance to the object from the film exceeds 3 meters, the system sensitivity is unsatisfactory and the film becomes under-exposure, leading to a defect that a satisfactorily finished photograph cannot be obtained.

The system sensitivity of film with a lens for outdoor photographing is determined by the F-number of the lens, the shutter speed, and the sensitivity of the preloaded photographic material, and that of film with a lens for indoor photographing is determined by the F-number of the lens, the guide number of the strobe, and the sensitivity of the preloaded photographic material.

If it is tried to increase the system sensitivity by making the F-number of the lens small, the so-called depth of field is decreased and the range of the distance that will fall in focus is decreased. To make up this defect, for example, attachment of an autofocusing mechanism is considered, but that leads to additional cost and increases the weight of the system under the present art, which inevitably cancels, for example, the inexpensiveness and handiness that are great merits of the film with a lens. As other means, use of a wide angle lens is considered to increase the depth of field relatively, but it inevitably decreases the magnification, which is not preferable except for special applications.

If it is tried to increase the system sensitivity by lowering the shutter speed, problems of camera-shake and subject shaking inevitably arise. The technique in which the guide number of the strobe for indoor photographing is increased is accompanied by high cost and an increase of the weight of the system under the present art, which inevitably cancels, for example, the inexpensiveness and handiness that are great merits of film with a lens.

Therefore, a photographic material high in sensitivity and satisfactory in image quality and preservability for use in the film with a lens is earnestly desired.

On the other hand, as high-speed negative films, super-high-speed photographic materials, for example with ISO ratings of 1000, 1600, and 3200, are sold from concerned companies, but they are not satisfactory in graininess, sharpness, and colorfulness as general photographic materials for the film with a lens. Further, high-speed photographic materials are high in deterioration of performance due to exposure to natural radiation, as described, for example, in JP-A ("JP-A" means unexamined published Japanese patent

application) No. 226650/1988, which is one of great reasons for the lack of satisfactory graininess.

One can purchase a product of film with a lens, for example, at tourist resorts and can enjoy photographing immediately even if a camera was not brought along. This handiness is one of major merits of film with a lens, and therefore products of film with a lens are often piled onto wagons or the like at a shop front under direct sunshine, so that there is a higher risk that the photographic material therein will be exposed to an atmosphere whose temperature rises very high.

Therefore, the photographic material therein is required to be stable under high temperature and is to be hardly susceptible to the influence of gases given off from the packaging material or the photographic material under high temperature.

With regard to such storage stability, it is difficult for a high-speed photographic material to be rendered satisfactorily stable.

SUMMARY OF THE INVENTION

Therefore, the first object of the present invention is to provide a photographic product that has a preloaded photographic material and is provided with an exposure function; that is high in sensitivity, excellent in image quality, and stable during storage.

These and other objects, advantages, features, and uses will become more apparent as the description proceeds, when considered with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an exploded perspective view of an example of a photographic product having been preloaded with a photographic material of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The objects of the present invention have been attained by providing a photographic product provided with an exposure function and preloaded with a photographic material, in which said photographic material comprises at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer, has a specific photographic sensitivity of 640 or more, contains 3.0 to 8.0 g/m 2 of silver in total content, and contains a palladium compound in an amount of 0.1 mg/m 2 or more in terms of palladium.

The photographic product provided with an exposure function and preloaded with a photographic material of the present invention is a photographic product having, for example, a photographing lens such as an aspherical lens or a single lens with an F-number of 8 or more; a shutter mechanism, for example an exposure mechanism with a fixed speed of 1/50 to 1/200 seconds; and a housing chamber (film roll chamber), which houses a rolled color photographic material loaded directly therein or being contained in a case. Preferably the photographic material is housed directly in said housing chamber. The photographic material may be contained in a patrone or a cartridge. Preferably the housing chamber is smaller than the chamber in which the film after the photographing is rolled and housed. Fig. 1 illustrates an exploded perspective view of the photographic product of the present invention (the view is the same as that shown in Fig. 1 of Japanese Patent Application No. 246978/1986). In Fig. 1, reference numeral 1 indicates a body base, 2 indicates a back plate, 5 indicates a film roll, 3 indicates a film roll chamber, and 4 indicates a patrone chamber. After photographing, the photographic material is rolled by operating, for example, a film advance knob, to be housed into another housing chamber (patrone chamber). To make the photographic product with a preloaded photographic material compact, it can be housed, far example, in a nonmetallic patrone or a special small-sized patrone, or it can be housed directly in the housing chamber, but if it uses a common development processing system as it is, preferably it is housed in a patrone that is the same as that used for a usual 35-mm film.

In the photographic product with a preloaded photographic material, provided with an exposure function of the present invention, a color photographic material having a specific photographic sensitivity of 640 or more, more preferably 800 or more, is needed to be loaded.

Herein the term "specific photographic sensitivity" refers to the sensitivity determined in accordance with the definition described in JP-A No. 226650/1988, which is similar to the ISO sensitivity that is an international standard and the sensitivity is obtained under conditions wherein the time from the exposure to the development processing is shortened and the development processing conditions are made constant so as to reduce the uncertainty of the value.

The photographic material preloaded in the photographic product of the present invention is a color photographic material having, on a support, at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, and at least one blue-sensitive emulsion layer. Preferably emulsion layers having the same color sensitivity, are made up of two or more emulsion layers different in sensitivity since the so-called graininess canceling effect can be used. More preferably emulsion layers having the same color sensitivity are made up of three or more emulsion layers different in sensitivity.

As described above, high-speed photographic materials are high in deterioration of performance due to exposure to natural radiation, as described, for example, in JP-A No. 226650/1988, which is one of the great reasons for the lack of satisfactory graininess. In order to reduce the influence due to exposure to natural radiation, it is effective to reduce the content of all the silver contained in the photographic material as much as possible.

The content of all the silver contained in the photographic material preloaded in the photographic product of the present invention is 3.0 to 8.0 g/m². A preferable range of the content of the silver varies depending, for example, on the layer constitution of the particular photographic material, the type of the coupler used, the type of the emulsion used, and the duration of the guaranteed performance at a particular storage place, and therefore it cannot be determined generally; but if the photographic material having a specific photographic sensitivity of 640 or more has a silver content of more than 8.0 g/m², deterioration of graininess is observed clearly when the photographic material in the form of a photographic-material-preloaded photographic product provided with an exposure function is stored for about 2 years in various conceivable places of shops, such as tourist resorts. If the photographic material having a specific photographic sensitivity of 640 or more has a silver content of less than 3.0 g/m², the latitude and the maximum density required for color negative photographic materials cannot be secured. Preferably the silver content is 3.0 to 7.5 g/m², more preferably 3.0 to 7.0 g/m².

In the case wherein emulsion layers identical in color-sensitivity and different sensitivity are to be made up of two or more emulsion layers, if the content of silver in the emulsion layer highest in sensitivity of the color sensitive layers is increased, the influence by the exposure to natural radiation becomes greater than the case wherein the content of silver in the emulsion layer lower in sensitivity is increased. Therefore, preferably the content of silver in the emulsion layer highest in sensitivity is not increased too much. The silver content is preferably 0.3 to 1.6 g/m^2 , more preferably 0.3 to 1.4 g/m^2 , and further more preferably 0.3 to 1.2 g/m^2 .

Preferably, in the photographic material preloaded in the photographic product provided with an exposure function of the present invention, at least one emulsion layer contains a tabular grain emulsion in which silver halide grains having an aspect ratio of 5 or more amount to 50% (area) or more in all the silver halide grains in the particular emulsion layer. Preferably the aspect ratio is 5 to 20, more preferably 5 to 12. A tabular emulsion in which the silver halide grains having an aspect ratio of 5 or more amount to preferably 60% (area) or more, more preferably 70% or more, in all the silver halide grains in the particular emulsion layer, is contained.

The term "tabular grain emulsion" refers to grains that are literally flat in appearance. An emulsion having twinning planes that are parallel to each other and (111) outer planes is well known, and a normal crystal emulsion having no twinning planes anisotropically grown is also known. As an example of the latter, tabular grains having (100) planes as described by Mignot et al. in <u>Journal of Cryst. Growth</u>, Vol. 23, page 207 (1974), are known.

In tabular grains, the term "aspect ratio" means the ratio of the diameter to the thickness; that is, the value obtained by dividing the diameter of the silver halide grain by the thickness. Herein the term "diameter" means the diameter of a circle having an area equal to the projected area of the silver halide grain observed under an optical microscope or electron microscope.

More preferably, a tabular emulsion wherein silver halide grains having an aspect ratio of 5 or more amount to 50% (area) in all the silver halide grains in the particular emulsion layer is contained in each of at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer, and at least one blue-sensitive emulsion layer in the photographic material.

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Particularly it is generally preferable that the emulsion in the blue-sensitive emulsion layer positioned furthest from the support be a tabular emulsion low in light scattering because this can increase the sharpness of the lower layer.

Since a tabular emulsion is high in specific surface (ratio of surface to volume), a larger amount of a sensitizing dye can be used, and since an emulsion high in sensitivity can be prepared with the grain size smaller, it is particularly preferable that a tabular emulsion is used in an emulsion layer particularly high in sensitivity out of a red-sensitive emulsion layer and a green-sensitive emulsion layer.

As described above, products of film with a lens are often piled onto wagons or the like at a shop front in tourist resorts or the like, under direct sunshine, so that there is a higher risk that the photographic product will be exposed to an atmosphere that will increase the temperature in the photographic product with a preloaded photographic material to a very high level. Therefore, the photographic material therein is required to be stable under high temperature and to be hardly susceptible to the influence of gases given off from the packaging material or the photographic material under high temperature. Due to such stability and particularly fogging increase during storage, it is very difficult to render enough stability to a photographic material high in sensitivity.

The inventors have studied keenly to solve this problem and have found that incorporation of a Pd (palladium) compound in an amount of $0.1~\text{mg/m}^2$ or more in terms of Pd into the photographic material has a specific effect on the stability when the photographic material is stored in the form of a photographic-material-preloaded photographic product. The amount is preferably $1~\text{mg/m}^2$ or more, more preferably $10~\text{mg/m}^2$ or more.

As the Pd compound, any Pd compound can be used, and examples include $(NH_4)_2 PdCl_4$, $PdCl_2$, $(NH_4)_2 PdBr_4$, and $Pd(NO_3)_2$.

The photographic material generally comprises a support, a backing layer, emulsion layers, a surface-protective layer, intermediate layers, and an antihalation layer, and the Pd compound of the present invention is applied by adding it directly or together with a suitable solvent or a binder independently to these layers. Generally, in many cases, the Pd compound is applied by adding it directly to the backing layer, the emulsion layers, the surface-protective layer, the intermediate layers, or the antihalation layer. Preferably the Pd compound is added to the emulsion layers, the surface-protective layers, or the intermediate layers, more preferably to the surface-protective layer or the intermediate layers.

To add the Pd compound, any method generally used when an additive is added to a photographic material can be applied. For example, in the case of a water-soluble compound, it is formed into an aqueous solution having a suitable concentration, and in the case of a water-insoluble or sparingly water-soluble compound, it is dissolved in a suitable organic solvent, such as alcohols, glycols, ketones, esters, and amides, which solvent is compatible with water and will not adversely affect the photographic characteristics, and the solution may be added.

Addition of a Pd compound to a silver halide photographic material is in itself known and is disclosed, for example, in U.S. Patent Nos. 2,448,060 and 2,472,631. However it was not known at all that the addition of a Pd compound to a photographic-material-preloaded photographic product that contains a specific color photographic material high in sensitivity, as disclosed in the present invention, exhibits a specific effect on stability under high temperature.

It is suitable that the photographic material to be used in the present invention is provided with at least one blue-sensitive silver halide emulsion layer, at least one green-sensitive silver halide emulsion layer, and at least one red-sensitive silver halide emulsion layer on a support and there is no particular restrictions on the number and order of the silver halide emulsion layers and the nonphotosensitive layers. A typical example is a silver halide photographic material having on a support at least one photosensitive layer that comprises a plurality of silver halide emulsion layers whose color sensitivities are substantially identical but whose sensitivities are different, the photosensitive layer being a unit photosensitive layer having color sensitivity to any of blue light, green light, and red light, and in a multilayer silver halide color photographic material, the arrangement of the unit photosensitive layers is generally such that a red-sensitive layer, a green-sensitive layer, and a blue-sensitive layer in the order stated from the support side are placed. However, the above order may be reversed according to the purpose and such an order is possible that layers having the same color sensitivity have a layer different in color sensitivity therefrom between them.

Nonphotosensitive layers such as various intermediate layers may be placed between, on top of, or under the above-mentioned silver halide photographic layers.

The intermediate layer may contain, for example, couplers and DIR compounds as described in JP-A Nos. 43748/1986, 113438/1984, 113440/1984, 20037/1986, and 20038/1986 and may also contain a color mixing inhibitor as generally used.

Each of the silver halide emulsion layers constituting unit photosensitive layers respectively can preferably take a two-layer constitution comprising a high-sensitive emulsion layer and a low-sensitive emulsion layer as described in West Germany Patent No. 1,121,470 or British Patent No. 923,045. Generally, they are arranged preferably such that the sensitivities are decreased toward the support and each nonphotosensitive layer may be placed between the silver halide emulsion layers. As described, for example, in JP-A No. 112751/1982, 200350/1987, 206541/1987, and 206543/1987, a low-sensitive emulsion layer may be placed away from the support and a high-sensitive emulsion layer may be placed nearer to the support.

A specific example of the order includes an order of a low-sensitive blue-sensitive layer (BL)/high-sensitive blue-sensitive layer (BH)/high-sensitive green-sensitive layer (GH)/low-sensitive green-sensitive layer (GL)/high-sensitive red-sensitive layer (RH)/low-sensitive red-sensitive layer (RL), or an order of BH/BL/GL/GH/RH/RL, or an order of BH/BL/GL/RH stated from the side away from the support.

As described in JP-B No. 34932/1980, an order of a blue-sensitive layer/GH/RH/GL/RL stated from the side away from the support is also possible.

Further as described in JP-A Nos. 25738/1981 and 63936/1987, an order of a blue-sensitive layer/GL/RL/GH/RH stated from the side away from the support is also possible.

Further as described in JP-B No. 15495/1974, an arrangement is possible wherein the uppermost layer is a silver halide emulsion layer highest in sensitivity, the intermediate layer is a silver halide emulsion layer lower in sensitivity than that of the uppermost layer, the lower layer is a silver halide emulsion layer further lower in sensitivity than that of the intermediate layer so that the three layers different in sensitivity may be arranged with the sensitivities successively lowered toward the support. Even in such a constitution comprising three layers different in sensitivity, an order of a medium-sensitive emulsion layer/high-sensitive emulsion layer/low-sensitive emulsion layer stated from the side away from the support may be taken in layers identical in color sensitivity as described in JP-A No. 202464/1984.

Further, for example, an order of a high-sensitive emulsion layer/low-sensitive emulsion layer/medium-sensitive emulsion layer or an order of a low-sensitive emulsion layer/medium-sensitive emulsion layer can be taken. In the case of more than three layers, the arrangement can be varied as above.

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In order to improve color reproduction, a donor layer (CL) having an interlayer effect that is different in spectral sensitivity distribution from that of main photosensitive layers, such as BL, GL, and RL, described in U.S. Patent Nos. 4,663,271, 4,705,744, and 4,707,436 and JP-A Nos. 160448/1987 and 89850/1988 is preferably arranged adjacent to or near to the main photosensitive layers.

As stated above, various layer constitutions and arrangements can be selected in accordance with the purpose of the particular photosensitive material.

A preferable silver halide to be contained in the photographic emulsion layer of the photographic material utilized in the present invention is silver iodobromide, silver iodochloride, or silver iodochlorobromide, containing about 30 mol% or less of silver iodide. A particularly preferable silver halide is silver iodobromide or silver iodochlorobromide, containing about 2 to about 10 mol% of silver iodide.

The silver halide grains in the photographic emulsion may have a regular crystal form, such as a cubic shape, an octahedral shape, and a tetradecahedral shape, or a irregular crystal shape, such as spherical shape or a tabular shape, or they may have a crystal defect, such as twin planes, or they may have a composite crystal form.

The silver halide grains may be fine grains having a diameter of about $0.2~\mu m$ or less, or large-size grains with the diameter of the projected area being down to about $10~\mu m$, and as the silver halide emulsion, a polydisperse emulsion or a monodisperse emulsion can be used.

The silver halide photographic emulsions that can be used in the present invention may be prepared suitably by known means, for example, by the methods described in I. Emulsion Preparation and Types, in Research Disclosure (RD) No. 17643 (December 1978), pp. 22 - 23, and ibid. No. 18716 (November 1979), p. 648, and ibid. No. 307105 (November, 1989), pp. 863 - 865; the methods described in P. Glafkides, Chimie et Phisique Photographique, Paul Montel (1967), in G.F. Duffin, Photographic Emulsion Chemistry, Focal Press (1966), and in V.L. Zelikman et al., Making and Coating of Photographic Emulsion, Focal Press (1964).

A monodisperse emulsion, such as described in U.S. Patent Nos. 3,574,628 and 3,655,394, and in British Patent No. 1,413,748, is also preferable.

The crystal structure of silver halide grains may be uniform, the outer halogen composition of the crystal structure may be different from the inner halogen composition, or the crystal structure may be layered. Silver halides whose compositions are different may be joined by the epitaxial joint, or a silver halide may be joined, for example, to a compound other than silver halides, such as silver rhodanide, lead oxide, etc. Mixture of grains having various crystal form may also be used.

Although the above-described emulsions may be either a surface latent image-type that forms latent image mainly on the surface, an internal latent image-type that forms latent image at the inner part of grain, or a type that forms latent image both on the surface and at the inner part of grain, it is necessary to be a negative-type emulsion. Of internal latent image-type emulsions, an internal latent image-type emulsion of core/shell-type grain, as described in JP-A No. 264740/1988, may be used. The preparation method of such internal latent image-type emulsion of core/shell-type grain is described in JP-A No. 133542/1984. The thickness of shell in such emulsion may be different according to a development process or the like, but a

range of 3 to 40 nm is preferable, and a range of 5 to 20 nm is particularly preferable.

The silver halide emulsion that has been physically ripened, chemically ripened, and spectrally sensitized is generally used. Additives to be used in these steps are described in Research Disclosure Nos. 17643, 18716 and 307105, and involved sections are listed in the Table shown below.

In the photographic material of the present invention, two or more kinds of emulsions in which at least one of characteristics, such as grain size of photosensitive silver halide emulsion, distribution of grain size, composition of silver halide, shape of grain, and sensitivity is different each other can be used in a layer in a form of mixture.

Silver halide grains the surface of which has been fogged as described in, for example, U.S. Patent No. 4,082,553, and silver halide grains or colloidal silver grains the inner part of which has been fogged as described in, for example, U.S. Patent No. 4,626,498 and JP-A No. 214852/1984 may be preferably used in a photosensitive silver halide emulsion layer and/or a substantially non-photosensitive hydrophilic colloid layer. "Silver halide grains the surface or inner part of which has been fogged" means a silver halide grains capable of being uniformly (non-image-wisely) developed without regard to unexposed part or exposed part to light of the photographic material. The method for preparing a silver halide grains the surface or inner part of which has been fogged are described, for example, in U.S. Patent No. 4,626,498 and JP-A No. 214852/1984.

The silver halide composition forming inner nucleus of core/shell-type silver halide grain the inner part of which has been fogged may be the same or different. As a silver halide grain the surface or inner part of which has been fogged, any of silver chloride, silver chlorobromide, silver bromoiodide, silver chloroiodobromide can be used. Although the grain size of such silver halide grains which has been fogged is not particularly restricted, the average grain size is preferably 0.01 to 0.75 μ m, particularly preferably 0.05 to 0.6 μ m. Further, the shape of grains is not particularly restricted, a regular grain or an irregular grain can be used, and although it may be a polydisperse emulsion, a monodisperse emulsion (that contains at least 95% of silver halide grains in weight or in number of grains having grain diameter within $\pm 40\%$ of average grain diameter) is preferable.

In the present invention, it is preferable to use a non-photosensitive fine grain silver halide. "Non-photosensitive fine grain silver halide" means a silver halide fine grain that does not expose at an imagewise exposure to light to obtain a color image and is not developed substantially at a development processing, and preferably it is not fogged previously.

Fine grain silver halide has a silver bromide content of 0 to 100 mol%, and may contain silver chloride and/or silver iodide, if needed. Preferable ones contain silver iodide of 0.5 to 10 mol%.

The average grain diameter (average diameter of circle corresponding to projected area) of fine grain silver halide is preferably 0.01 to 0.5 μ m, more preferably 0.02 to 0.2 μ m.

The fine grain silver halide can be prepared in the same manner as an ordinary photosensitive silver halide. In this case, it is not necessary to optically sensitize the surface of the silver halide grain and also spectrally sensitizing is not needed. However, before adding this to the applying solution, to add previously such a compound as triazoles, azaindenes, benzothiazoliums, and mercapto compounds or a known stabilizing agent, such as zinc compounds, is preferable. Colloidal silver is preferably contained in a layer containing this fine grain silver halide.

Known photographic additives that can be used in the present invention are also described in the abovementioned three Research Disclosures, and involved sections are listed in the same Table below.

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5	RD 307105 ovember 1989)	99		pp.866-868	89	pp.868-870	73	72	72	pp.874-875	pp.873-874	92	pp.875-876	pp.876-877	pp.878-879
10	RD 3071((November	p.866	1		b.868	bb.	p.873	p.872	p.872	·dd	·dd	p.876	· dd	·dd	pp.
15	RD 18716 (November 1979)	p.648 (right column)	p.648 (right column)	pp.648 (right column) -649 (right column)	p.647 (right column)	(right column)	pp.649 (right column) -650 (left column)	p.650 (left to right column)	p.650 (left column)	(left column)	(left column)	(right column)	(right column)	p.650 (right column)	
20	RD 1 (Novemb	p.648 (ri	p.648 (ri	pp.648 (1 -649 (ric	p.647 (r)	p.649 (r	pp.649 (1-650 (1e)	p.650 (16 column)	p.650 (10	p.651 (lo	p.651 (10	p.650 (r.	р.650 (г	p.650 (r	1
25	RD 17643 cember 1978)	3	1	pp.23-24	4	pp.24-25	pp.25-26	p.25 (right column)	5	9	9	7	pp.26-27	7	1
30	RD 1764 (December	p.23	·	·dd	p.24	· dd	·dd	p.2 col	p.25	p.26	p.26	p.27	. dd	p.27	
35		ır	ing agent	ers ers	70	70	ilter cbers	agent	sers			Lubricants	ıd agents		
40	Additive	sensitizer	Sensitivity-enhancing	Spectral sensitizers and Supersensitizers	ing agents	Antifogging agents and Stabilizers	absorbers, Filter and UV Absorbers	Stain-preventing a	dye stabiliz	Ñ		and	aids and active ag	ic agents	agent
45	Ad	Chemical	Sensitiv	Spectral and Supe	Brightening	Antifogg and Stab	Light ab dyes, an	Stain-pr	Image dy	Hardeners	Binders	Plasticizers	Coating aids an Surface-active	Antistatic	Matting
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Further, in order to prevent the lowering of photographic performances due to formaldehyde gas, a compound described in, for example, U.S. Patent Nos. 4,411,987 and 4,435,503 that is able to react with formaldehyde to immobilize is preferably added to the photographic material.

In the photographic material of the present invention, a mercapto compound described in, for example, U.S. Patent Nos. 4,740,454 and 4,788,132, and JP-A Nos. 18539/1987 and 283551/1989 is preferably contained.

In the photographic material of the present invention, a compound that releases a fogging agent, a development accelerator, a solvent for silver halide, or the precursor thereof, independent of the amount of silver formed by a development processing, described in, for example, JP-A No. 106052/1989 is preferably contained.

In the photographic material of the present invention, a dye dispersed by a method described in, for example, International Publication No. WO88/04794 and Japanese Published Searched Patent Publication No. 502912/1989, or a dye described in, for example, European Patent No. 317,308A, U.S. Patent No. 4,420,555, and JP-A No. 259358/1989 is preferably contained.

In the present invention, various color couplers can be used, and concrete examples of them are described in patents cited in the above-mentioned Research Disclosure No. 17643, VII-C to G, and ibid. No. 307105, VII-C to G.

As yellow couplers, those described in, for example, U.S. Patent Nos. 3,933,501, 4,022,620, 4,326,024, 4,401,752, and 4,248,961, JP-B No. 10739/1983, British Patent Nos. 1,425,020 and 1,476,760, U.S. Patent Nos. 3,973,968, 4,314,023, and 4,511,649, and European Patent No. 249,473A are preferable.

As magenta couplers, 5-pyrazolone-type compounds and pyrazoloazole-type compounds are preferable, and couplers described in, for example, U.S. Patent Nos. 4,310,619 and 4,351,897, European Patent No. 73,636, U.S. Patent Nos. 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June 1984), JP-A No. 33552/1985, Research Disclosure No. 24230 (June 1984), JP-A Nos. 43659/1985, 72238/1986, 35730/1985, 118034/1980, and 185951/1985, U.S. Patent Nos.4,500,630, 4,540,654 and 4,556,630, and International Publication No. WO88/04795 are preferable, in particular.

As cyan couplers, phenol-type couplers and naphthol-type couplers can be mentioned, and those described in U.S. Patent Nos. 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171, 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011, and 4,327,173, West German Patent Application (OLS) No. 3,329,729, European Patent Nos. 121,365A and 249,453A, U.S. Patent Nos. 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212, and 4,296,199, and JP-A No. 42658/1986 are preferable. Further, pyrazoloazole series couplers as described, for example, in JP-A Nos. 553/1989, 554/1989, 555/1989, and 556/1989, and imidazole series couplers as described, for example, in U.S. Patent No. 4,818,672 can be used.

Typical examples of polymerized dye-forming coupler are described in, for example, U.S. Patent Nos. 3,451,820, 4,080,211, 4,367,282, 4,409,320, and 4,576,910, British Patent No. 2,102,137, and European Patent No. 341,188A.

As a coupler which forms a dye having moderate diffusibility, those described in U.S. Patent No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570, and West German Patent Application (OLS) No. 3,234,533 are preferable.

As a colored coupler to rectify the unnecessary absorption of color-forming dyes, those couplers described in, paragraph VII-G of Research Disclosure No. 17643, paragraph VII-G of ibid. No. 307105, U.S. Patent No. 4,163,670, JP-B No. 39413/1982, U.S. Patent Nos. 4,004,929 and 4,138,258, and British Patent No. 1,146,368 are preferable. Further, it is preferable to use couplers to rectify the unnecessary absorption of color-forming dyes by a fluorescent dye released upon the coupling reaction as described in U.S. Patent No. 4,774,181 and couplers having a dye precursor, as a group capable of being released, that can react with the developing agent to form a dye as described in U.S. Patent No. 4,777,120.

A compound that releases a photographically useful residue accompanied with the coupling reaction can be used favorably in this invention. As a DIR coupler that release a development retarder, those described in patents cited in paragraph VII-F of the above-mentioned Research Disclosure No. 17643 and in paragraph VII-F of ibid. No. 307105, JP-A Nos. 151944/1982, 154234/1982, 184248/1985, 37346/1988, and 37350/1986, and U.S. Patent Nos. 4,248,962 and 4,782,012 are preferable.

A coupler that releases a bleaching accelerator, described, for example, in Research Disclosure Nos. 11449 and 24241, and JP-A No. 201247/1986, is effective for shortening the time of processing that has bleaching activity, and the effect is great in the case wherein the coupler is added in a photographic material using the above-mentioned tabular silver halide grains.

As a coupler that releases, imagewisely, a nucleating agent or a development accelerator upon developing, those described in British Patent Nos. 2,097,140 and 2,131,188, and JP-A Nos. 157638/1984 and 170840/1984 are preferable. Further, compounds which release a fogging agent, a developing accelerator, or a solvent for silver halide by a oxidation-reduction reaction with the oxidized product of developing agent as described in JP-A Nos. 107029/1985, 252340/1985, 44940/1989, and 45687/1989 are also preferable.

Other compounds that can be incorporated in the photographic material of the present invention include competitive couplers described in U.S. Patent No. 4,130,427, multi-equivalent couplers described in U.S.

Patent Nos. 4,283,472, 4,338,393, and 4,310,618, couplers which release a DIR redox compound, couplers which release a DIR coupler, and redox compounds which release a DIR coupler or a DIR redox as described in JP-A Nos. 185950/1985 and 24252/1987, couplers which release a dye to regain a color after releasing as described in European Patent Nos. 173,302A and 313,308A, couplers which release a ligand as described in U.S. Patent No. 4,555,477, couplers which release a leuco dye as described in JP-A No. 75747/1988, and couplers which release a fluorescent dye as described in U.S. Patent No. 4,774,181.

Couplers utilized in the present invention can be incorporated into a photographic material by various known dispersion methods.

Examples of high-boiling solvent for use in oil-in-water dispersion process are described in, for example, U.S. Patent No. 2,322,027.

As specific examples of high-boiling organic solvent having a boiling point of 175°C or over at atmospheric pressure for use in oil-in-water dispersion process can be mentioned phthalates (e.g., dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decyl phthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, and bis(1,1-diethylpropyl)phthalate), esters of phosphoric acid or phosphonic acid (e.g., triphenyl phosphate, tricrezyl phosphate, 2-ethylhexyldiphenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate, and di-2-ethylhexylphenyl phosphate), benzoic esters (e.g., 2-ethylhexyl benzoate, dodecyl benzoate, and 2-ethylhexyl-p-hydroxy benzoate), amides (e.g., N,N-diethyldodecanamide, N,Ndiethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-tamyl phenol), aliphatic carbonic acid esters (e.g., bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributylate, isostearyl lactate, and trioctyl citrate), aniline derivertives (e.g., N,N-dibutyl-2-butoxy-5-t-octylaniline), and hydrocarbons (e.g., paraffin, dodecyl benzene, and diisopropyl naphthalene). Further, as a co-solvent an organic solvent having a boiling point of about 30 °C or over, preferably a boiling point in the range from 50 °C to about 160 °C can be used, and as typical example can be mentioned ethyl acetate, butyl acetate, ethyl propionate, methylethyl ketone, cyclohexanone, 2-ethoxyethyl acetate, and dimethyl formamide.

Specific examples of process and effects of latex dispersion method, and latices for impregnation are described in, for example, U.S. Patent No. 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

In the photographic material of this invention, various antiseptics and antifungal agents, such as phenetyl alcohol, and 1,2-benzisothiazoline-3-one, n-butyl-p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, and 2-(4-thiazolyl)bezimidazole as described in JP-A Nos. 257747/1988, 272248/1987, and 80941/1989 are preferably added.

Suitable supports to be used in this invention are described in, for example, in the above-mentioned Research Disclosure No. 17643, page 28, No. 18716, from page 647, right column to page 648, left column and No. 307105, page 879.

In the photographic material of the present invention, preferably the total layer thickness of all the hydrophilic colloid layers on the side having emulsion layers is 28 μ m or below, more preferably 23 μ m or below, further more preferably 18 μ m or below, and particularly preferably 16 μ m or below. Preferably the film swelling speed $T_{1/2}$ is 30 sec or below, more preferably 20 sec or below. The term "layer thickness" means layer thickness measured after moisture conditioning at 25 °C and a relative humidity of 55% for two days, and the film swelling speed $T_{1/2}$ can be measured in a manner known in the art. For example, the film swelling speed $T_{1/2}$ can be measured by using a swellometer (swell-measuring meter) of the type described by A. Green et al. in Photographic Science and Engineering, Vol. 19, No. 2, pp. 124-129, and $T_{1/2}$ is defined as the time required to reach a film thickness of 1/2 of the saturated film thickness that is 90% of the maximum swelled film thickness that will be reached when the film is treated with a color developer at 30 °C for 3 min 15 sec.

The film swelling speed $T_{1/2}$ can be adjusted by adding a hardening agent to the gelatin that is a binder or by changing the time conditions after the coating. Preferably the ratio of swelling is 150 to 400%. The ratio of swelling is calculated from the maximum swelled film thickness obtained under the above conditions according to the formula: (Maximum swelled film thickness - film thickness)/Film thickness.

It is preferable that the photographic material of the present invention is provided a hydrophilic layer (designated as a back layer) having a total dried layer thickness of 2 μ m to 20 μ m at the opposite side of having emulsion layers. In such back layer, it is preferable to be contained the above-mentioned light-absorbent, filter-dye, UV-absorbent, static preventer, film-hardener, binder, plasticizer, lubricant, coating auxiliary, and surface-active agent. The ratio of swelling of back layer is preferably 150 to 500%.

The color photographic material in accordance with the present invention can be subjected to the development processing by an ordinary method as described in the above-mentioned RD No. 17643, pp.

28-29, ibid. No. 18716, p. 651, from left column to right column, and ibid. No. 307105, pp. 880 - 881.

Preferably, the color developer used for the development processing of the photographic material of the present invention is an aqueous alkaline solution whose major component is an aromatic primary amine color-developing agent. As the color-developing agent, aminophenol compounds are useful, though p-phenylene diamine compounds are preferably used, and typical examples thereof include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -methoxyethylaniline, and their sulfates, hydrochlorides, and p-toluenesulfonates. Of these, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline sulfate is paticularly preferable. A combination of two or more of these compounds may be used in accordance with the purpose.

The color developer generally contains, for example, buffers, such as carbonates, borates or phosphates of alkali metals, and development inhibitors or antifoggants, such as chloride salt, bromide salts, iodide salts, benzimidazoles, benzothiazoles, or mercapto compounds. The color developer may, if necessary, contain various preservatives, such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines for example N,N-biscarboxymethylhydrazine, phenylsemicarbazides, triethanolamine, and catecholsulfonic acids, organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol, polyethylene glycol, quaternary ammonium salts, and amines, dye forming couplers, competing couplers, auxiliary developers such as 1-phenyl-3-pyrazolidone, tackifiers, and various chelate agents as represented by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids, and phosphonocarboxylic acids, typical example thereof being ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N',N'-tetramethylenephosphonic acid, and ethylenediamine-di(o-hydroxyphenylacetic acid), and their salts.

If reversal processing is carried out, it is common that after black and white development and reversal processing are carried out, the color development is carried out. As the black and white developers, known black and white developing agents, such as dihydroxybenzenes, for example hydroquinone, 3-pyrazolidones, for example 1-phenyl-3-pyrazolidone, and aminophenols, for example N-methyl-paminophenol, can be used alone or in combination.

Generally the pH of this color developer and black-and-white developing solution is 9 to 12. The replenishing amount of these developing solutions is generally 3 liter or below per square meter of the color photographic material to be processed, though the replenishing amount changes depending on the type of color photographic material, and if the concentration of bromide ions in the replenishing solution is lowered previously, the replenishing amount can be lowered to 500 ml or below per square meter of the color photographic material. If it is intended to lower the replenishing amount, it is preferable to prevent the evaporation of the solution and oxidation of the solution with air by reducing the area of the solution in processing tank that is in contact with the air.

The contact area of the photographic processing solution with the air in the processing tank is represented by the opened surface ratio which is defined as follows:

Opened surface

ratio (cm⁻¹)

Contact surface area (cm²) of the processing solution with the air

Whole volume (cm³) of the processing solution

40

wherein "contact surface area of the processing solution with the air" means a surface area of the processing solution that is not covered by anything such as floating lids or rolls.

The opened surface ratio is preferably 0.1 cm⁻¹ or less, more preferably 0.001 to 0.05cm⁻¹. Methods for reducing the opened surface ratio that can be mentioned include a utilization of movable lids as described in JP-A No. 82033/1989 and a slit-developing process as described in JP-A No. 216050/1988, besides a method of providing a shutting materials such as floating lids on the surface of photographic processing solution of processing tank. It is preferable to adopt the means for reducing the opened surface ratio not only in a color developing and black-and-white developing process but also in all succeeding processes, such as bleaching, bleach-fixing, fixing, washing, and stabilizing process. It is also possible to reduce the replenishing amount by using means of suppressing the accumulation of bromide ions in the

developer.

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Although the processing time of color developing is settled, in generally, between 2 and 5 minutes, the time can be shortened by, for example, processing at high temperature and at high pH, and using a color developer having high concentration of color developing agent.

The photographic emulsion layer are generally subjected to a bleaching process after color development

The beaching process can be carried out together with the fixing process (bleach-fixing process), or it can be carried out separately from the fixing process. Further, to quicken the process bleach-fixing may be carried out after the bleaching process. In accordance with the purpose, the process may be arbitrarily carried out using a bleach-fixing bath having two successive tanks, or a fixing process may be carried out before the bleach-fixing process, or a bleaching process may be carried out after the bleach-fixing process. As the bleaching agent, use can be made of, for example, compounds of polyvalent metals, such as iron (III), peracids, quinones, nitro compounds. As typical bleaching agent, use can be made of organic complex iron (III), such as complex salts of aminopolycarboxylic acids, for example ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid, citric acid, tartaric acid, and malic acid. Of these, aminopolycarboxylic acid iron (III) complex salts, including ethylenediaminetetraacetic acid iron (III) complex salts and 1,3-diaminopropanetetraacetic acid iron (III) complex salt are preferable in view of rapid-processing and the prevention of pollution problem. Further, aminopolycarboxylic acid iron (III) complex salts are particularly useful in a bleaching solution as well as a bleach-fixing solution. The pH of the bleaching solution or the bleach-fixing solution using these aminopolycarboxylic acid iron (III) complex salts is generally 4.0 to 8.0, by if it is required to quicken the process, the process can be effected at a low pH.

In the bleaching solution, the bleach-fixing solution, and the bath preceding them a bleach-accelerating agent may be used if necessary. Specific examples of useful bleach-accelerating agents are compounds having a mercapto group or a disulfide linkage, described in U.S. Patent No. 3,893,858, West German Patent Nos. 1,290,812 and 2,059,988, JP-A Nos. 32736/1978, 57831/1978, 37418/1978, 72623/1978, 95630/1978, 95631/1978, 104232/1978, 124424/1978, 141623/1978, and 28426/1978, and Research Disclosure No. 17129 (July, 1978); thiazolidine derivatives, described in JP-A No. 140129/1975; thiourea derivatives, described in JP-B No. 8506/1970, JP-A Nos. 20832/1977 and 32735/1978, and U.A. Patent No. 3,706,561; iodide salts, described in West German Patent No. 1,127,715 and JP-A No. 16235/1983; polyoxyethylene compounds in West German Patent Nos. 966,410 and 2,748,430; polyamine compounds, described in JP-B No. 8836/1970; other compounds, described in JP-A Nos. 40943/1974, 59644/1974, 94927/1978, 35727/1979, 26506/1980, and 163940/1983; and bromide ions. Of these, compounds having a mercapto group or a disulfide group are preferable in view of higher acceleration effect, and in particular, compounds described in U.A. Patent No. 3,893,858, West German Patent No. 1,290,812, and JP-A No. 95630/1978 are preferable. Further, compound described in U.S. Patent No. 4,552,834 are preferable. These bleach-accelerating agents may be added into a photographic material. When the color photographic materials for photographing are to be bleach-fixed, these bleach-accelerating agents are particularly effective.

In addition to the above compounds, preferably the bleaching solution and the bleach-fixing solution contain an organic acid in order to prevent bleach stain. Particularly preferable organic acids are compounds having an acid dissociation constant (pKa) of 2 to 5 and specifically, for example, acetic acid and propionic acid are preferable.

As the fixing agent used in the fixing solution and the bleach-fixing solution, for example, thiosulfates, thiocyanates, thioether compounds, thioureas, and large amount of iodide salts can be mentioned, thiosulfates are generally used, and particularly ammonium thiosulfate can be most widely used. A combination of a thiosulfate with a thiocyanate, a thioether compound, a thiourea, or the like is also preferably used. As the preservative of the fixing solution and the bleach-fixing solution, a sulfite, a carbonyl-bisulfinic acid adduct, or a sulfinic acid compound described in European Patent No. 294769A is preferable. Further, to the fixing solution and the bleach-fixing solution, various aminopolycarboxylic acids and organic phosphonic acids are preferably added in order to stabilize the solution.

In the present invention, to the fixing solution or the bleach-fixing solution is added preferably a compound having a pKa of 6.0 to 9.0 in order to adjust the pH and preferably imidazoles, such as imidazole, 1-methylimidazole, 1-ethylimidazole, and 2-methylimidazole, are added in an amount of 0.1 to 10 mol/liter.

With respect to the total time of the desilvering step, the shorter the total time is within the range wherein silver retention does not occur, the more preferable it is. Preferably, it is 1 to 3 min, more

preferably 1 to 2 min. Further, the processing temperature is 25 to 50 °C, preferably 35 to 45 °C. In a preferable temperature range, the desilvering speed can be improved and stain can be prevented effectively from occurring after the processing.

In the desilvering step, the stirring is preferably intensified as far as possible. Specific means of intensifying the stirring include a method described in JP-A No. 183460/1987 wherein a jet of a processing solution is struck against the emulsion surface of a photographic material, a method described in JP-A No. 183461/1987 wherein the stirring effect is increased by using a rotating means, a method wherein a photographic material is moved with the emulsion surface in contact with a wiper blade placed in a solution so that the emulsion surface is made turbulent to improve the stirring effect, and a method wherein the circulated amount of the whole of a processing solution is increased. Such a stirring improving means is effective for any of the bleaching solution, the bleach-fixing solution, and the fixing solution. It appears that the improvement in stirring quickens the supply of the bleaching agent and the fixing agent into the emulsion coating and as a result the desilvering speed is increased. The above stirring improving means is effective when a bleach accelerator is used, and the acceleration effect can be increased remarkably or the fixing hindering effect by the bleach accelerator can be removed.

The automatic processor used in processing the photographic material used in the present invention has preferably a photographic material carrying means described in JP-A Nos. 191257/1985, 191258/1985, and 191259/1985. As described in the above JP-A No. 191257/1985, such a conveying means can reduce remarkably the carry-in of the processing solution to a bath from the preceding bath and therefore is high in the effect in preventing the performance of the processing solution from being deteriorated. Such an effect is particularly effective in shortening the processing time in each step and in reducing the replenishing amount of the processing solution.

It is common for the silver halide color photographic material of the present invention to undergo, after a desilvering process such as fixing or bleach-fixing, a washing step and/or a stabilizing step. The amount of washing water may be set within a wide range depending on the characteristics (e.g., due to the materials used, such as couplers), the application of the photographic material, the washing temperature, the number of washing tanks (the number of steps), the type of replenishing system, including, for example, the counter-current system and the direct flow system and other various conditions. Of these, the relationship between the number of water-washing tanks and the amount of washing water in the multi-stage counter current system can be found according to the method described in Journal of the Society of Motion Picture and Television Engineers, Vol. 64, pages 248 to 253 (May 1955).

According to the multi-stage-counter-current system described in the literature mentioned above, although the amount of washing water can be considerably reduced, bacteria propagate with an increase of retention time of the washing water in the tanks, leading to a problem with the resulting suspend matter adhering to the photographic material. In processing the color photographic material of the present invention, as a measure to solve this problem the method of reducing calcium ion and magnesium ion described in JP-A No. 288838/1987 can be used quite effectively. Also chlorine-type bactericides such as sodium chlorinated isocyanurate, cyabendazoles, isothiazolone compounds described in JP-A No. 8542/1982, benzotriazoles, and other bactericides described by Hiroshi Horiguchi in Bokin Bobai-zai no Kagaku, (1986) published by Sankyo-Shuppan, Biseibutsu no mekkin, Sakkin, Bobaigijutsu (1982) edited by Eiseigijutsu-kai, published by Kogyo-Gijutsu-kai, and in Bokin Bobaizai Jiten (1986) edited by Nihon Bokin Bobai-gakkai, can be used.

The pH of the washing water used in processing the photographic material of the present invention is 4 to 9, preferably 5 to 8. The washing water temperature and the washing time to be set may vary depending, for example, on the characteristics and the application of the photographic material, and they are generally selected in the range of 15 to 45 °C for 20 sec to 10 min, and preferably in the range of 25 to 40 °C for 30 sec to 5 min. Further, the photographic material of the present invention can be processed directly with a stabilizing solution instead of the above washing. In such a stabilizing process, any of known processes, described in JP-A Nos. 8543/1982, 14834/1983, and 220345/1985 can be applied.

In some cases, the above washing process is further followed by stabilizing process, and as an example thereof can be mentioned a stabilizing bath that is used as a final bath for color photographic materials for photography, which contains a dye-stabilizing agent and a surface-active agent. As an example of dye-stabilizing agent can be mentioned aldehyde (e.g., formalin and gultalaldehyde), N-methylol compound, hexamethylenetetramine and aldehyde-sulfite adduct. In this stabilizing bath, each kind of the chelating agents and bactericides may be added.

The over-flowed solution due to the replenishing of washing solution and/or stabilizing solution may be reused in other steps, such as a desilvering step.

When each of the above-mentioned processing solutions is concentrated due to the evaporation of water in the processing using an automatic processor, preferably water to correct the concentration is added into each solution.

The silver halide color photographic material of the present invention may contain therein a color-developing agent for the purpose of simplifying and quickening the process. To contain such a color-developing agent, it is preferable to use various precursor for color-developing agent. For example, indoaniline-type compounds described in U.S. Patent No. 3,342,597, Schiff base-type compounds described in U.S. Patent No. 3,342,599 and Research Disclosure Nos. 14850 and 15159, aldol compounds described in Research Disclosure No. 13924, and metal salt complexes described in U.S. Patent No. 3,719,492, and urethane-type compounds described in JP-A No. 135628/1978 can be mentioned.

For the purpose of accelerating the color development, the silver halide color photographic material of the present invention may contain, if necessary, various 1-phenyl-3-pyrazolicones. Typical compounds are described in JP-A Nos. 64339/1981, 144547/1982, and 115438/1983.

The various processing solutions used for the present invention may be used at 10 to 50 °C. Although generally a temperature of 33 to 38 °C may be standard, a higher temperature can be used to accelerate the process to reduce the processing time, or a lower temperature can be used to improve the image quality or the stability of the processing solution.

Further, the silver halide photographic material of the present invention can be adopted to photographic materials for heat development described in, for example, U.S. Patent No. 4,500,626, JP-A Nos. 133449/1985, 218443/1984, and 238056/1986, and European Patent No. 210,660A2.

The photographic product having been preloaded with a photographic material of the present invention contains a color photographic material high in sensitivity, excellent in image quality, and stable at the time of storage and since the photographic product of the present invention has an exposure function, it can serve as a film with lens which can well exhibit its function inexpensively and conveniently.

Next, the present invention will be described in detail in accordance with examples, but the invention is not limited to them.

Reference example 1

Layers having compositions shown below were applied successively one over another on a cellulose triacetate film support with an under coat to prepare a multilayer color photographic material, Film 101.

Major materials used in the layers are classified as follows:

(Compositions of photosensitive layers)

35

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ExC: Cvan coupler

UV: Ultraviolet absorbent ExM: Magenta coupler

HBS: High boiling organic solvent

ExY: Yellow coupler
H: Gelatin hardener
ExS: Sensitizing dye

The figures for the components represent coated amounts in g/m^2 , the coated amount of the silver halide is given in terms of silver, and the coated amount of the sensitizing dye is given in mol for 1 mol of the silver halide in the same layer.

(Sample 101)

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First layer: Halation preventing layer				
Black colloidal silver	silver 0.18			
Gelatin	1.40			
ExM-1	0.18			
ExF-1	2.0×10^{-3}			
HBS-1	0.20			

Second layer: Intermediate layer					
Emulsion G	silver	0.065			
2,5-di-t-pentadecylhydroquinone		0.18			
ExC-2		0.020			
UV-1		0.060			
UV-2		0.080			
UV-3		0.10			
HBS-1		0.10			
HBS-2		0.020			
Gelatin		1.04			

Third layer: Low sensitivity red-sensitive emulsion layer				
Emulsion A	silver 0.25			
Emulsion C	silver 0.25			
ExS-1	4.5 × 10 ⁻⁴			
ExS-2	1.5 x 10 ⁻⁵			
ExS-3	4.5 × 10 ⁻⁴			
ExC-1	0.17			
ExC-3	0.030			
ExC-4	0.10			
ExC-5	0.005			
ExC-7	0.0050			
ExC-8	0.020			
Cpd-2	0.025			
HBS-1	0.010			
Gelatin	0.87			

Fourth layer: Medium sensitivity red-sensitive emulsion layer				
Emulsion D	silver 0.80			
ExS-1	3.0×10^{-4}			
ExS-2	1.2 x 10 ⁻⁵			
ExS-3	4.0×10^{-4}			
ExC-1	0.15			
ExC-2	0.060			
ExC-4	0.11			
ExC-7	0.0010			
ExC-8	0.025			
Cpd-2	0.023			
HBS-1	0.010			
Gelatin	0.75			

Fifth layer: High sensitivity red-sensitive emulsion layer				
Emulsion E	silver 1.70			
ExS-1	2.0×10^{-4}			
ExS-2	1.0×10^{-5}			
ExS-3	3.0×10^{-4}			
ExC-1	0.095			
ExC-3	0.040			
ExC-6	0.020			
ExC-8	0.007			
Cpd-2	0.050			
HBS-1	0.22			
HBS-2	0.10			
Gelatin	1.20			

Sixth layer: Intermediate layer				
Cpd-1 0.10				
0.50				
1.10				

Seventh layer: Low sensitivity green-sensitive emulsion layer				
Emulsion A	silver 0.17			
Emulsion B	silver 0.17			
ExS-4	4.0 x 10 ⁻⁵			
ExS-5	1.8 x 10 ⁻⁴			
ExS-6	6.5 x 10 ⁻⁴			
ExM-1	0.010			
ExM-2	0.33			
ExM-3	0.086			
ExY-1	0.015			
HBS-1	0.30			
HBS-3	0.010			
Gelatin	0.73			

Eighth layer: Medium sensitivity green-sensitive emulsion layer				
Emulsion D	silver 0.80			
ExS-4	2.0 x 10 ⁻⁵			
ExS-5	1.4 x 10 ^{−4}			
ExS-6	5.4 x 10 ⁻⁴			
ExM-2	0.16			
ExM-3	0.045			
ExY-1	0.01			
ExY-5	0.030			
HBS-1	0.16			
HBS-3	8.0 x 10 ⁻³			
Gelatin	0.90			

Ninth layer: High sensitivity green-sensitive emulsion layer				
Emulsion E	silver 1.70			
ExS-4	3.7 x 10 ^{−5}			
ExS-5	8.1 x 10 ⁻⁵			
ExS-6	3.2 × 10 ^{−4}			
ExC-1	0.010			
ExM-1	0.015			
ExM-4	0.040			
ExM-5	0.019			
Cpd-3	0.020			
HBS-1	0.25			
HBS-2	0.10			
Gelatin	1.20			

Tenth layer: Yellow filter layer				
Yellow colloidal silver	silver	0.010		
Cpd-1 HBS-1		0.16		
HBS-1		0.60		
Gelatin		0.60		

Eleventh layer: Low sensitivity blue-sensitive emulsion layer				
Emulsion C	silver 0.25			
Emulsion D	silver 0.40			
ExS-7	8.0 x 10 ⁻⁴			
ExY-1	0.030			
ExY-2	0.55			
ExY-3	0.25			
ExY-4	0.020			
ExC-7	0.01			
HBS-1	0.35			
Gelatin	1.30			

Twelfth layer: High sensitive	ity blue-sensitive emulsion layer
Emulsion F	silver 1.38
ExS-7	3.0 x 10 ⁻⁴
ExY-2	0.10
ExY-3	0.10
HBS-1	0.070
Gelatin	0.86

Thirteenth layer:	First protective layer
Emulsion G	silver 0.20
UV-4	0.11
UV-5	0.17
HBS-1	5.0 x 10 ⁻²
Gelatin	1.00

Fourteenth layer: Second p	protective layer
H-1	0.40
B-1 (diameter 1.7 μm)	5.0 x 10 ⁻²
B-2 (diameter 1.7 μm)	0.10
B-3	0.10
S-1	0.20
Gelatin	1.20

Further, in order to improve stability, processing property, pressure resistance, keeping property from mold and fungi, antistatic property, and coating property, besides above-mentioned components, W-1 to W-3, B-4 to B-6, F-1 to F-17 and iron salt, lead salt, gold salt, platinum salt, iridium salt, rhodium salt are optionally contained in all emulsion layers.

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Table 1

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		() () () () () () () () () ()	Deviation		Ratio of silver amount	er amount	
Emulsion	Average Average AgI grain content diameter (%) (µm)	Average grain diameter (µm)		Ratio of diameter/ thickness	<pre>[core/ intermediate/ shell]</pre>	(AgI content %)	Structures/ features of grains
A	1.5	0.30	10	1	[1/1]	(1/2)	Double structure cubic grains
В	1.5	0.50	æ	1	[1/1]	(1/2)	Double structure, cubic grains
υ	3.0	0.45	25	7	[10/60/30]	(0/1/8)	Triple structure, tabular grains
D	2.8	0.62	18	9	[14/56/30]	(0.2/1/7.5)	(0.2/1/7.5) Triple structure, tabular grains
ជ	2.3	0.83	16	9	[6/64/30]	(0.2/1/5.5)	(0.2/1/5.5) Triple structure, tabular grains
[24 .	13.6	1.30	26	m	[1/2]	(41/0)	Double structure, tabular grains
უ	1.0	0.07	15	1			Uniform structure, fine grains

In Table 1:

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- (1) Emulsions A to F were subjected to reduction sensitization using thiourea dioxide and thiosulfonic acid in accordance with Examples given in JP-A No. 191938/1990 when the grains were prepared.
- (2) Emulsions A to F were subjected to gold sensitization, sulfur sensitization, and selenium sensitization using in the presence of sodium thiocyanate and spectrally sensitizing dyes stated for the respective photosensitive layers in accordance with Examples given in JP-A No. 237450/1991.
- (3) In the preparation of tabular grains, low-molecular weight gelatins were used in accordance with Examples given in JP-A No. 158426/1989.
- (4) Rearrangement lines as described in JP-A No. 237450/1991 were observed in the tabular grains under a high-voltage electron microscope.

Compounds added to the layers are shown below.

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 $E \times C - 1$

$$E \times C - 2$$

OH CONHC₁₂H₂₅(n)

OH NHCOCH₃

OCH₂CH₂0
$$\longrightarrow$$
 N=N

Na0SO₂ SO₃Na

$$E \times C - 3$$

$$\begin{array}{c|c} \text{OH} & \text{CONH(CH}_2)_3\text{OC}_{12}\text{H}_{25}(n) \\ \hline \\ \text{(i)C}_4\text{H}_3\text{OCONH} & \text{OCH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H} \end{array}$$

$$E \times C - 4$$

OH
$$CONH(CH_2)_3O$$
 $C_5H_{11}(t)$ $(i)C_4H_9OCNH$

 $E \times C - 5$

CH₃ C₉H₁₉(n)

OH

CONHCH₂CHOCOCHC₇H₁₅(n)

CH₃

CH₃

CONH₂

HO

N

COOH

ExC-6

OH
$$CONH(CH_2)_3O$$
 $C_5H_{11}(t)$ C_5H_{11}

 $E \times C - 7$

$$(t)C_{5}H_{11} - OCH_{2}CONH$$

$$(t)C_{5}H_{11} + HO$$

$$(t)C_{5}H_{$$

 $E \times C - 8$

ExM-1

ExM-2

CH₂ CH₂ CH₂ CH CH₂ CH

CH₂ CH

CH₂ CH

CH₂ CH

CH₂ CH

CH₂ CH n = 50 m = 25 m' = 25 m' = 25 m' = 25 mol. wt. about 20,000

E xM-3

25 $C_{2}H_{5}$ -0CHCONH $C_{1}_{5}H_{3}_{1}$ NH N=N $-NHCOC_{4}H_{9}(t)$ $C_{1}_{5}H_{3}_{1}$ $C_{1}_{5}H_{3}_{1}$

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$$ExM-4$$

CH₂ Cl
$$0(CH_2)_20C_2H_5$$

$$C_5H_{11}(t)$$

$$CH_3$$

$$0(CH_2)_20C_2H_5$$

$$C_5H_{11}(t)$$

$$C_6H_{13}$$

ExM-5

$$0(CH_2)_{2}0 \qquad N \qquad 0 \qquad -0CH_3$$

$$CH_2NHSO_2 \qquad C_5H_{11}(t)$$

$$CH_3 \qquad NHCOCHO \qquad C_5H_{11}(t)$$

$E \times Y - 1$

 $CH_{3} CH_{2} CH_{3} COOCHCOOC COOCHCOOC$

$$ExY-2$$

 $CH_{3}O \xrightarrow{COCHCONH} \xrightarrow{COC} COCHCONH$ C1 C1 $C2H_{5}O$ CCHCONH C1 C1 C1 C1 C1 CH_{2} CH_{2}

$$ExY-3$$

$$C_2H_5$$
 C_2H_5
 C_2H_5

E x Y - 4

$$ExY-5$$

$$C(CH_3)_3 COCHCONH \longrightarrow C1 CH_3$$

$$C(CH_3)_3 COCHCONH \longrightarrow C1 CH_3$$

$$E \times F - 1$$

C1
$$CH_3$$
 CH_3 CH_3 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5

C2H50S030

$$Cpd-1$$

$$\begin{array}{c} C_6H_{1\,3}(n) \\ \\ OH \\ \\ OH \\ \\ OH \\ \end{array}$$

$$\begin{array}{c} C_6H_{1\,3}(n) \\ \\ \\ NHCOCHC_8H_{1\,7}(n) \\ \\ \\ C_6H_{1\,3}(n) \\ \end{array}$$

$$Cpd-2$$

$$(t)C_4H_9 \xrightarrow{OH} CH_2 \xrightarrow{OH} C_4H_9(t)$$

$$CH_3 \xrightarrow{CH_3} CH_3$$

$$Cpd-3$$

UV-1

$$CI$$
 OH $C_4H_9(t)$ $(t)C_4H_9$

UV-2

UV-4

$$\begin{array}{c} CH_{3} \\ CH_{2} \\ CD_{2}CH_{2}CH_{2}OCO \\ NC \end{array} \begin{array}{c} CH_{3} \\ CD_{2}CH_{3} \\ CD_{2}CH_{3} \\ CD_{2}CH_{3} \\ CD_{2}CH_{3} \end{array}$$

$$x : y = 70 : 30 \text{ (wt\%)}$$

$$UV-5$$

$$(C_2H_5)_2NCH=CH-CH=C < CO_2C_8H_{17}$$

HBS-1 Tricresyl phosphate

HBS-2 Di-n-butyl phtarate

HBS-3
$$(t)C_5H_{11}$$
 C_2H_5 $(t)C_5H_{11}$ C_2H_5

ExS-1

$$\begin{array}{c|c}
C_2H_5 \\
\hline
C_2H_5
\end{array}$$

$$=CH-C=CH$$

$$(CH_2)_3SO_3N_2$$

$$(CH_2)_4SO_3 = C1$$

ExS-2

$$\begin{array}{c} C_{2}H_{5} \\ \\ C_{2}H_{5} \\ \\ CH_{2})_{3}SO_{3} \\ \\ CH_{2})_{3}SO_{3}H \cdot N(C_{2}H_{5})_{3} \\ \end{array}$$

 $E \times S = 3$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{1}CCH=C-CH=C$$

$$C_{1}CH_{2}CH_{3}SO_{3}C$$

$$C_{2}H_{5}$$

$$C_{2}H_{5}$$

$$C_{1}CH_{2}CH_{2}CH_{3}SO_{3}H\cdot N$$

ExS-4

C₂H₅

$$C_2H_5$$

$$CH_3$$

$$CH_2$$

$$CH_2$$

$$CH_3$$

$$CH_2$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

$$CH_3$$

ExS-5

$$\begin{array}{c} C_2H_5 \\ \hline \\ CH_2)_4SO_3 \\ \hline \end{array}$$

ExS-6

ExS-7

S-1

$$0 = \begin{matrix} H & & \\ N & & \\ N & & \\ N & & \\ H & & \\ H & & \\ \end{matrix}$$

H-1

$$CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$$

$$CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$$

¹⁰ B-1

B-2

$$\begin{array}{cccc} CH_3 & CH_3 \\ \hline -(-CH_2-C-\frac{1}{2}-CH_2-C-\frac{1}{2}-\frac{1}{2}-CH_2-\frac{1}{2}-\frac{1}{2} \\ COOH & COOCH_3 \end{array}$$

B-3

$$(CH_3)_3SiO \xrightarrow{CH_3} (CH_3)_3$$

$$(CH_2)_2g \xrightarrow{CH_3} (CH_3)_3$$

$$(CH_3)_4g \xrightarrow{CH_3} (CH_3)_4g \xrightarrow{CH_3} (CH_$$

B-4

$$\begin{array}{c} -\text{CH}_2 - \text{CH} \xrightarrow{}_{\mathbf{z}} \\ \text{SO}_3 \text{Na} \end{array}$$

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B-5

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 $\begin{array}{cccc}
-\left(\text{CH}_2 - \text{CH} \right)_{x} & \left(-\text{CH}_2 - \text{CH} \right)_{y} & x/y = 70/30 \\
N & O & OH
\end{array}$

B-6

 $\frac{-\left(-CH_2-CH_2\right)}{N}$ (mol. wt. about 10,000)

W-1

C₈F₁₇SO₂NHCH₂CH₂CH₂OCH₂CH₂N(CH₃)₃ CH₃—SO₃ $\stackrel{\bigcirc}{\bigcirc}$

W-2

 C_8H_{17} — C_8H_{17} — CCH_2CH_2 — CCH_2 — CCH_2CH_2 — CCH_2 — CCH_2CH_2 — CCH_2 — CCH_2CH_2 — CCH_2CH_2 — CCH_2CH_2 — CCH_2CH_2 — CCH_2 — CC

W-3

Na0₃S $C_4H_9(n)$ $C_4H_9(n)$

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$$F-1$$

F-2 N-N SH COONa

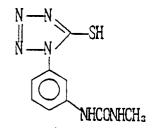
F-4

F - 3

F-5

F-7

F-6



$$F-9$$

F-10

5

(n)C₆H₁ 3NH NHOH

NHC₆H₁₃(n)

10

$$F-11$$

F - 12

15

CH₂ N N

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20

$$F - 13$$

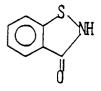
F - 14

30

$$F - 15$$

F-16

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OCH2CH2OH

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F-17

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Samples 102 to 104 were prepared in the same manner as Sample 101, except that the grain sizes of Emulsions D, E, and F were changed as shown in Table 2.

The specific photographic sensitivities of the Samples were measured and the results are shown in Table 2.

The Samples were cut and worked to form two groups, each consisting of the same samples; each of the Samples of one group was housed in a common metal patrone and was contained in an Asahi Pentax ME Super (a single-lens reflex camera, manufactured by Asahi Kogaku); and each of the Samples of the other group was rolled as shown in Fig. 1 and was housed directly in a film roll chamber of photographic product which is a film with a lens, to produce a photographic product having been preloaded with a

photographic material provided with an exposure function (the F-number of the lens used was 13.8; the focal distance was 35 mm; and the shutter speed was set at 1/100 sec).

Using them, photographs were taken outdoors in fine weather, in cloudy weather, and in the evening in cloudy weather, and after they were developed in the same manner as used for the determination of the specific photographic sensitivity, printing was carried out on a color paper in a usual manner. The results of organoleptic evaluation of the obtained pictures are shown in Table 3. It can be understood that, in the case wherein the single-lens reflex camera having an exposure-adjusting function was used, all the photographic materials showed that the finish was satisfactory, whereas in the case of the photographic product having been preloaded with a photographic material without an exposure-adjusting function, Sample 101, low in specific photographic sensitivity, gave, in the dark, only a dull feeble picture. Accordingly, in the case of a photographic product provided with an exposure function, it is preferable to build in a color photographic material having a specific photographic sensitivity of 640 or more.

Table 2

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Sample 101 102 103 104 0.62 Emulsion D (µm) 0.68 0.73 0.80 Emulsion E (µm) 0.83 0.93 1.05 1.15 Emulsion F (µm) 1.30 1.45 1.6 1.80 Specific photographic sensitivity 420 550 724 950

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α	3
٥	4

	Sing	Single-lens reflex camera	reflex ca	ımera	Photog.	raphic pro a photogra	Photographic product preloaded with a photographic material	ided [a]
	101	102	103	104	101	102	103	104
In fine weather	satis- faction	satis- satis- faction faction	satis- faction	satis- faction	satis- faction	satis- faction	satis- faction	satis- faction
In cloudy weather		satis- satis- faction faction	satis- faction	satis- faction	slightly dull	nearly satis- faction	satis- faction	satis- faction
In the evening in cloudy weather	satis- faction	satis- faction	satis- faction	satis- faction	dark finish since sensiti-vity is not enough	a dull feeble picture	nearly satis- faction	satis- faction

Example 1

Samples 205 to 207 were prepared in the same manner of the procedure as that for Sample 104 in Reference Example 1, except that the coated amount of silver in the fourth layer, the fifth layer, the eighth

layer, the ninth layer, and the twelfth layer was changed as shown in Table 4.

The Samples were loaded in photographic-material-preloaded photographic products in the same manner as in Reference Example 1 and were stored for 18 months in a manner similar to that shown in JP-A No. 226650/1988 in a lead block in a refrigerator wherein the effect of natural radiation could be almost ignored (storage conditions A) and in a refrigerator in Osaka branch office of Fuji Photo Film Co., Ltd. wherein the environmental radiation dose was 80 mR/year (storage conditions B).

Thereafter, the photographic materials were taken out and the sensitometry and RMS with the exposure amount being 0.001 lux•sec were determined in the same manner as that for the specific photographic sensitivity. The results are shown in Table 5.

It can be understood that, in all the photographic materials having a silver content of 3.0 to 8.0 g/m² according to the present invention, the fogging increase due to environmental radiation, the lowering of the sensitivity, and the deterioration of graininess could be reduced.

Table 4

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			Sample	
	104 Comparative example (g/m²)	205 This invention (g/m²)	206 This invention (g/m²)	207 This invention (g/m²)
The 4th layer	0.80	0.80	0.60	0.80
The 5th layer	1.70	1.50	1.40	1.20
The 8th layer	0.80	0.80	0.60	0.80
The 9th layer	1.70	1.50	1.40	1.20
The 12th layer	1.38	1.38	1.15	1.15
Content of all the silver	8.325	7.925	7.095	7.095

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Table 5

		Compa	04 cative	20! Thi		200 Thi		20° Th: inve	
		A	В	A	В	A	В	A	В
Sensi	tivity	*							
	blue	100	80	100	80	92	83	92	83
	green	100	75	97	85	92	84	86	83
	red	100	70	98	83	93	82	87	81
	.ric graphi .tivity		689	926	798	879	789	822	779
Foggi	ng (Dm	in)							
	blue	0.90	1.02	0.90	1.02	0.88	0.96	0.88	0.96
	green	0.60	0.75	0.59	0.69	0.59	0.67	0.56	0.65
	red	0.30	0.48	0.29	0.38	0.28	0.35	0.26	0.33
RMS									
	blue	0.032	0.041	0.032	0.041	0.030	0.036	0.030	0.03
	green	0.020	0.032	0.019	0.026	0.018	0.023	0.018	0.02
	red	0.018	0.029	0.017	0.024	0.017	0.022	0.017	0.02

Note: * Sensitivities are represented with the relative values of storage condition A of Sample 104 as is 100.

Example 2

Samples 308 to 311 were prepared in the same manner as the procedure for Sample 206 in Example 1, except that in the sixth layer, the tenth layer, and the thirteenth layer, respectively, $Na_2PdCl_4 \cdot 3H_2O$ as shown in Table 6 (the amount being in terms of Pd) was contained. The Samples were loaded in photographic products in the same manner as that of Reference Example 1, and after storing them in a refrigerator and in a 60 °C and 60% RH air-conditioned room for five days, the sensitometry was carried out in the same manner as in Example 1. The results are shown in Table 7. It can be understood that the cases containing 0.1 mg/m² or more of Pd in photographic materials, wherein the fogging increase during storage can be distinctly reduced, is very preferable.

Table 6

			Sampl	е	
(206 mg/m ²)	308 (mg/m ²)(309 (mg/m ²)	310 (mg/m ²)	311 (mg/ m
Applied amount of Pd The 6th layer	0	0	0	0	25
The 10th layer	0	0	0	0	25
The 13th layer	0	0.5	5	50	0

				Table 7					
206		308	8	309	6	310	0	311	1
Refrige- ration 6	၁.0	Refrige- ration	J.09	Refrige- ration	٥,09	Refrige- ration	ວ.09	Refrige- ration	٥°09
;	.10	0.89	1.01	0.88	0.97	0.88	0.94	0.89	0.95
0.	.79	0.58	0.70	0.59	0.67	0.59	0.65	0.58	0.64
0	.44	0.28	0.37	0.29	0.34	0.28	0.32	0.29	0.31

55 Example 3

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Samples 412 to 415 were prepared in the same manner as the procedure in Example 2, based on Sample 206 of Example 1, except that $Na_2PdCl_4.3H_2O$ was added to the layers shown in Table 8 in the

amounts shown in Table 8 in terms of Pd. Each of Samples 206, 308 to 311, and 412 to 415 was built in each of photographic product in a similar manner to Example 2 and after subjecting to moisture conditioning at 25 °C and 60% RH, each product was packaged in a sealed wrapping paper container lined with aluminum. Separately, each of Samples was housed in a metal patrone, and after subjecting to moisture conditioning at 25 °C and 60% RH, each patrone was housed in a sealed container for use the usual 135 form.

After one group made up of the thus prepared two forms of package and container having Samples 206, 308 to 311, and 412 to 415 was stored in a refrigerator for 10 days and the other group made up of the same as the above was stored in an air-conditioned room at 50°C and 60% RH for 10 days, the sensitometry was carried out similarly to Example 1. The results are shown in Table 9.

It can be understood that similarly to Example 2, the addition of Pd in an amount of 0.1 mg/m² or more reduced very favorably the fogging at the time of storage, which effect was particularly noticeable in the form of a photographic product with a preloaded photographic material, that the addition to the emulsion layer reduced favorably the fogging at the time of storage but lowered a little the sensitivity, and that the addition to the surface protective layer and the intermediate layer was more favorable.

Table 8

_	_	
2	n	

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Sample	Layer added of Pd	Added amount of Pd(mg/m²)		
206 308 309	- The 13th layer (Surface protective layer) The 13th layer (Surface protective layer)	0 0.5 5		
310	The 13th layer (Surface protective layer) The 6th layer (Intermediate layer)	50 25		
311	The 10th layer (Intermediate layer = Yellow filter layer)	25		
412	The 2nd layer (Intermediate layer)	50		
413	The 5th layer (High-sensitive red-sensitive emulsion layer)	5		
414	The 5th layer (High-sensitive red-sensitive emulsion layer)	50		
415	The 12th layer (High-sensitive blue-sensitive emulsion layer)	5		

Table 9

Sample No.	Forms of wrapping at storage*	Fogging		Relative sensitivity**			
		Blue	Green	Red	Blue	Green	Red
206	A	0.88	0.58	0.28	100	100	100
	B	1.08	0.76	0.40	50	60	58
	C	1.00	0.70	0.35	75	80	78
308	A	0.89	0.58	0.28	101	100	99
	B	1.03	0.70	0.37	60	65	63
	C	0.98	0.69	0.34	80	81	79
309	A	0.88	0.59	0.29	99	101	100
	B	0.96	0.65	0.33	93	91	92
	C	0.97	0.64	0.33	92	91	92
310	A	0.88	0.59	0.28	100	99	100
	B	0.92	0.62	0.31	95	94	96
	C	0.92	0.62	0.31	94	95	95
311	A	0.89	0.58	0.29	100	100	101
	B	0.91	0.63	0.30	94	95	95
	C	0.92	0.62	0.31	94	94	96
412	A B C	0.88 0.93 0.93	0.58 0.63 0.64	0.28 0.32 0.31	99 93 94	100 94 93	99 95
413	A	0.89	0.59	0.26	101	99	90
	B	0.97	0.65	0.32	92	92	80
	C	0.96	0.65	0.33	92	91	79
414	A	0.89	0.59	0.22	101	101	65
	B	0.92	0.62	0.29	94	95	60
	C	0.91	0.62	0.29	94	94	61
415	A	0.86	0.58	0.28	85	100	101
	B	0.96	0.63	0.32	73	91	91
	C	0.97	0.63	0.32	74	91	92

Note; *A: Two forms of wrapping, below-mentioned B and C, stored in refrigerator. Figures of A mean the average value of two wrapping forms, since the

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results were nearly equal.

- B: Photographic product with a preloaded photographic material form, stored at 50°C and 60% RH.
- C: Usual 135 form, stored at 50°C and 60% RH.
- **: Sensitivity of Sample 206 at form A is set to 100

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

Claims

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- 1. A photographic product provided with an exposure function and preloaded with a photographic material, in which said photographic material comprises at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer, has a specific photographic sensitivity of 640 or more, contains 3.0 to 8.0 g/m² of silver in total content, and contains a palladium compound in an amount of 0.1 mg/m² or more in terms of palladium.
- 2. The photographic product as claimed in claim 1, wherein each of said red-sensitive emulsion layer, green-sensitive emulsion layer, and blue-sensitive emulsion layer in said photographic material is respectively consisted of two or more layers having each other different sensitivities wherein the silver content of an emulsion layer highest in sensitivity is 0.3 to 1.6 g/m².
- 35 3. The photographic product as claimed in claim 1, wherein, in at least one emulsion layer of said photographic material, tabular silver halide grains having an aspect ratio of 5 or more are contained in an amount of 50% (area) or more based on all the silver halide grains of said emulsion layer.
- 4. The photographic product as claimed in claim 1, wherein, in at least one emulsion layer of each redsensitive emulsion layer, green-sensitive emulsion layer, and blue-sensitive emulsion layer of said
 photographic material, respectively, tabular silver halide grains having an aspect ratio of 5 or more are
 contained in an amount of 50% (area) or more based on all the silver halide grains of said emulsion
 layer.
- 5. The photographic product as claimed in claim 1, wherein the total silver content of said photographic material is 3.0 to 7.5 g/m^2 .
 - **6.** The photographic product as claimed in claim 2, wherein the silver content of emulsion layer highest in sensitivity is 0.3 to 1.4 g/m².
 - 7. The photographic product as claimed in claim 3, wherein the aspect ratio of tabular grains is 5 to 20.
- 8. The photographic product as claimed in claim 3, wherein the tabular grains having an aspect ratio of 5 or more are contained in an amount of 60% (area) or more based on all the silver halide grains of said emulsion layer.
 - 9. The photographic product as claimed in claim 4, wherein the aspect ratio of tabular grains is 5 to 20.

- **10.** The photographic product as claimed in claim 4, wherein the tabular grains having an aspect ratio of 5 or more are contained in an amount of 60% (area) or more based on all the silver halide grains of said emulsion layer.
- **11.** The photographic product as claimed in claim 1, wherein the amount of palladium compound contained in said photographic material is 1 mg/m² or more in terms of palladium.
 - **12.** The photographic product as claimed in claim 1, wherein the palladium compound is contained in an emulsion layer, a surface protective layer, or an intermediate layer of said photographic material.
 - **13.** The photographic product as claimed in claim 1, wherein the palladium compound is selected from the group consisting of (NH₄)₂PdCl₄, PdCl₂, (NH₄)₂PdBr₄, and Pd(NO₃)₂.

