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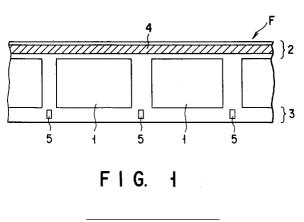
# Silver halide color photographic light-sensitive material.

(c) A silver halide color photographic light-sensitive material have at least one hydrophilic colloid layer containing a compound represented by Formula (A) below on a support consisting of a belt-like polyester base:

Formula (A) A-(Time)<sub>n</sub>-W

wherein A represents a group capable of releasing  $(Time)_n$ -W upon reacting with an oxidized form of a color developing agent, Time represents a timing group, W represents a group which exhibits a development inhibiting effect after released from  $(Time)_n$ -W, and <u>n</u> represents 1, 2, or 3. Four or less perforations are formed per frame in one or both of side edge portions of the polyester base, the area of an imaging area is 3.0 cm<sup>2</sup> to 7.0 cm<sup>2</sup>, and the aspect ratio of the imaging area is 1.40 to 2.50. This light-sensitive material can form a color image excellent in image qualities, particularly sharpness and color reproducibility and can thereby decrease the thickness of a support, making miniaturization of a cartridge possible without impairing image qualities.





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The present invention relates to a silver halide color photographic light-sensitive material to be used as a color photographic film of a format different from conventional formats, in which image qualities, particularly sharpness and color reproducibility are improved and the area of an imaging area and the number of perforations are specified.

- 5 Recently, a wider variety of photographs have been able to be obtained owing to improvements in graininess, sharpness, and color reproducibility of color photographic light-sensitive materials for photographing (including color negative films and color reversal light-sensitive materials; to be generally referred to simply as color negative films hereinafter) together with the spread of cameras incorporating zoom lenses or bifocal lenses.
- A camera having a zoom lens or a bifocal lens, however, is increased in size with the increase in focal length on the telephoto side, resulting in a poor portability. When miniaturization of the camera is given priority, on the other hand, no sufficient telephoto effect can be imparted to the camera.

As means for solving the above problems, U.S. Patents 3,490,844, 4,583,831, and 4,650,304, for example, have proposed techniques of so-called pseudo zooming by focusing attention on the advance in performance of recent color negative films. In this pseudo zooming technique, information about the focal length of a lens, which is input to a film during photographing by some means, is detected in the stage of printing to enlarge portions of an imaging area of a negative film, thereby obtaining the telephoto effect.

This pseudo zooming technique has been developed for silver halide color negative roll films contained in 135-format cartridges which are mainly used in recent years.

20 Miniaturization of a lens can be expected by the use of the pseudo zooming technique because the focal length of the lens can be shortened by this technique. The technique, however, requires a lens with an image circle corresponding to the 135 format and also makes it difficult to realize a camera much more compact than current 135-format cameras because of the use of a cartridge corresponding to the 135 format. In addition, the pseudo zooming technique is also unpreferable in terms of resource saving because

25 the ratio of an effective area of an imaging area used in formation of prints to an overall film area is reduced. Furthermore, a variation in image quality between prints obtained from the same film is one of complaints of users.

To solve the above problems, it is most effective to decrease the size of the image circle of a lens besides decreasing the area of the imaging area of a color negative film. As a result of market research concerning image qualities of prints, however, it is found that general users do not accept any product unless degradation in image qualities (graininess and sharpness) of prints resulting from the decrease in area of an imaging area of a film is improved. In particular, a demand for an improvement in sharpness is strong.

- It is generally known that development inhibitor releasing couplers (so-called DIR couplers) have an effect of improving the sharpness of a color negative film. These couplers are described in, e.g., the patents described in Research Disclosure (RD) No. 17643, items VII to F, JP-A-57-151944 ("JP-A" means Published Unexamined Japanese Patent Application), JP-A-57-154234, JP-A-60-184248, JP-A-60-37346, and U.S. Patent 4,248,962. However, the effect of these couplers is still unsatisfactory for small-format color negative products which requires larger print magnifications.
- As means for improving image qualities, on the other hand, each of JP-A-2-273743 and JP-A-2-273744 discloses a color negative film set in a cartridge, which contains a compound represented by Formula (A) below and releasing a precursor of a development inhibitor, and in which the effective area and the aspect ratio (the ratio of the lateral length to the longitudinal length) of an imaging area of each frame to be exposed are defined:
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# Formula (A) A-(Time)<sub>n</sub>-W

wherein A represents a group capable of releasing  $(Time)_n$ -W upon reacting with the oxidized form of a color developing agent, Time represents a timing group, W represents a group which exhibits a development inhibiting effect after released from  $(Time)_n$ -W, and n represents 1, 2, or 3.

In addition, JP-A-3-078742 discloses a photographic film package in which a color negative film containing a compound which is represented by Formula (A) above and releases a precursor of a development inhibitor is packed in a flatness holding cartridge. Although color negative films with improved image qualities have begun to be provided by these methods, the qualities of the films are still unsatisfactory.

As a support (base) for a color negative film, cellulose triacetate (to be abbreviated as TAC hereinafter) is generally used. This TAC base has no optical anisotropy and hence has a high transparency. The TAC base also has an excellent property of eliminating curling once formed after development because it has a

high water absorption. When a film is stored in the form of a roll over long periods of time, however, curling remains strongly, and the resulting low flatness during photographing largely interferes with the achievement of sharpness that the color negative film has. In addition, this high water absorption leads to a high humidity dependency, with the result that the state of curling at photographing changes in accordance with the form of a roll. This gives rise to a problem of inskillty

5 the humidity at which the film is stored in the form of a roll. This gives rise to a serious problem of inability to obtain a constant image quality. The TAC base also has a drawback of a low dynamic strength.

For these reasons, in a color negative film with a small format which has a small area of an imaging area and hence requires a high enlargement ratio, total improvements involving not only an improvement in sharpness of light-sensitive layers themselves but also improvements in a support constituting the color negative film and in the processed form of the color negative material as a photographic film are important

to achieve high image qualities.

It is, therefore, an object of the present invention to provide a silver halide color photographic lightsensitive material which is totally improved in image qualities, particularly sharpness and color reproducibility by taking into account not only light-sensitive layers but also a support constituting the light-sensitive material and the processed form of the material.

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The above object of the present invention is achieved by a silver halide color photographic lightsensitive material having at least one hydrophilic colloid layer containing a compound represented by Formula (A) below on a support, wherein the support comprises a belt-like polyester base, four or less perforations are formed per frame in one or both of side edge portions of the polyester base, the area of an imaging area is  $3.0 \text{ cm}^2$  to  $7.0 \text{ cm}^2$ , and the aspect ratio of the imaging area is 1.40 to 2.50:

### Formula (A) $A-(Time)_n-W$

wherein A represents a group capable of releasing (Time)<sub>n</sub>-W upon reacting with the oxidized form of a color developing agent, Time represents a timing group, W represents a group which exhibits a development inhibiting effect after released from (Time)<sub>n</sub>-W, and n represents 1, 2, or 3.

In the silver halide color photographic light-sensitive material according to the present invention, the image qualities, particularly the sharpness and the color reproducibility of the resultant color images are improved, and the support can be made thin. This makes it possible to reduce the area of an imaging area without impairing the image qualities and to decrease the size of a cartridge. Therefore, the silver halide

color photographic light-sensitive material of the present invention is useful in miniaturizing cameras.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a plan view showing a part of the construction of one embodiment of a film manufactured from the light-sensitive material of the present invention, in which one rectangular perforation is formed per frame in one side edge portion of the film;

Fig. 2 is a plan view showing a part of the construction of another embodiment of a film manufactured from the light-sensitive material of the present invention, in which one rectangular perforation is formed per frame in one side edge portion of the film;

Fig. 3 is a plan view showing a part of the construction of still another embodiment of a film manufactured from the light-sensitive material of the present invention, in which two circular perforations are formed per frame in each side edge portion of the film;

Fig. 4 is a plan view showing a part of the construction of still another embodiment of a film manufactured from the light-sensitive material of the present invention, in which two rectangular perforations are formed per frame in one side edge portion of the film;

Fig. 5 is a plan view showing a part of the construction of still another embodiment of a film manufactured from the light-sensitive material of the present invention, in which two perforations are formed per frame in each side edge portion of the film, perforations formed in one side edge portion are rectangular, and those formed in the other side edge portion are circular;

Fig. 6 is a plan view showing a part of the construction of still another embodiment of a film manufactured from the light-sensitive material of the present invention, in which three perforations are formed per frame in one side edge portion of the film, and these perforations are circular and triangular; Fig. 7 is a plan view showing a part of the construction of still another embodiment of a film

manufactured from the light-sensitive material of the present invention, in which three perforations are formed per frame in each side edge portion of the film, and these perforations are circular and rectangular;

Fig. 8 is a plan view showing a part of the construction of still another embodiment of a film manufactured from the light-sensitive material of the present invention, in which four elliptic perforations

are formed per frame in each side edge portion of the film; and

Fig. 9 is a sectional view showing the section in the direction of thickness of the film shown in each of Figs. 1 to 8.

A polyester base used as the support of a silver halide color photographic light-sensitive material according to the present invention will be described first.

As a method of reducing curling in a polyester film, the method described in JP-A-51-16358, i.e., the method of performing heating at a temperature lower by 30 °C to 50 °C than the glass transition temperature (Tg) is known. The glass transition temperature is defined as, when a 10-mg portion of a sample film is heated at a rate of 20 °C/min in a helium-nitrogen stream by using a differential scanning calorimeter (DSC), an arithmetic mean temperature of a temperature at which an output signal begins to deviate from a base line and a temperature at which it arrives at a new base line. If an endothermic peak appears, however, a temperature indicating the maximum value of this endothermic peak is defined as Tg.

When this technique was applied to a film wound with a large diameter (14 mm), such as a conventional

135-size magazine, and a film wound with a small diameter (10 mm), it was surprising to find that a curl reduction ratio of the film wound with the diameter of 10 mm exhibited an unexpectedly larger value than that of the film wound with the diameter of 14 mm. The curl reduction ratio is a value calculated by (true core set curl/absolute core set curl) × 100. The "core set" is to cause curling by winding a film around a spool, and the "core set curl" means curling caused in the longitudinal direction by the core set. The degree of curling is measured in accordance with Test Method A in ANSI/ASC PH1. 29-1985 and

20 represented in terms of 1/R [m] (R is the radius of a curl). The true core set curl is a value calculated by (absolute core set curl) - (controlled core set curl). The absolute core set curl means the core set curl of a photographic film before curling is improved. The controlled core set curl means the core set curl of a photographic film after curling is improved.

It is desirable to perform a heat treatment at as a high temperature as possible because this effect can be achieved within a short time period when the heat treatment is performed at high temperatures. The effect, however, disappears when the treatment temperature exceeds Tg, and is significant when the temperature is essentially 50 °C or more. Therefore, the heat treatment is preferably performed at temperatures between 50 °C and Tg.

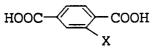
In addition, the effect appears from a treatment time of 0.1 hour or more. Although the effect is 30 enhanced as the treatment time is prolonged, the effect is saturated for a treatment time of 1,500 hours or more.

Furthermore, since the effect disappears at a temperature of Tg or more, it is desirable to perform the heat treatment after subbing and coating of a back layer and before coating of emulsions. This is so because the support is normally processed at a high temperature of 180 °C or more in these coating steps,

- <sup>35</sup> but the Tg's of many general-purpose polyester materials are lower than that. On the other hand, since the heat treatment is performed at a high temperature of 50°C or more for a long period of time, the performance of emulsion layers is degraded if the heat treatment is performed after coating of the emulsion layers. Therefore, the heat treatment is preferably performed before coating of emulsion layers.
- As described above, the effect disappears when exposed to high temperatures exceeding Tg. Since, 40 therefore, the temperatures in automobiles under the blazing sun in summer rise up to nearly 90°C, polyester preferably has Tg of 90°C or more when these actual use conditions of users are taken into account.

There exists no polyester, on the other hand, which is versatile and transparent and yet has Tg exceeding 200 °C. Therefore, a preferable Tg is 90 °C to 200 °C.

- <sup>45</sup> Polyester with a glass transition temperature of 90 °C or more, which is used as the support in the present invention, can be formed from, e.g., diol and dicarboxylic acid. Usable examples of dicarboxylic acid are terephthalic acid, isophthalic acid, phthalic acid, phthalic anhydride, succinic acid, glutaric acid, adipic acid, sebacic acid, succinic anhydride, maleic acid, fumaric acid, maleic anhydride, itaconic acid, citraconic anhydride, tetrahydro phthalic anhydride, diphenylene-p,p'-dicarboxylic acid, tetrachloro phthalic
- anhydride, 3,6-endomethylenetetrahydro phthalic anhydride, 1,4-cyclohexanedicarboxylic acid,

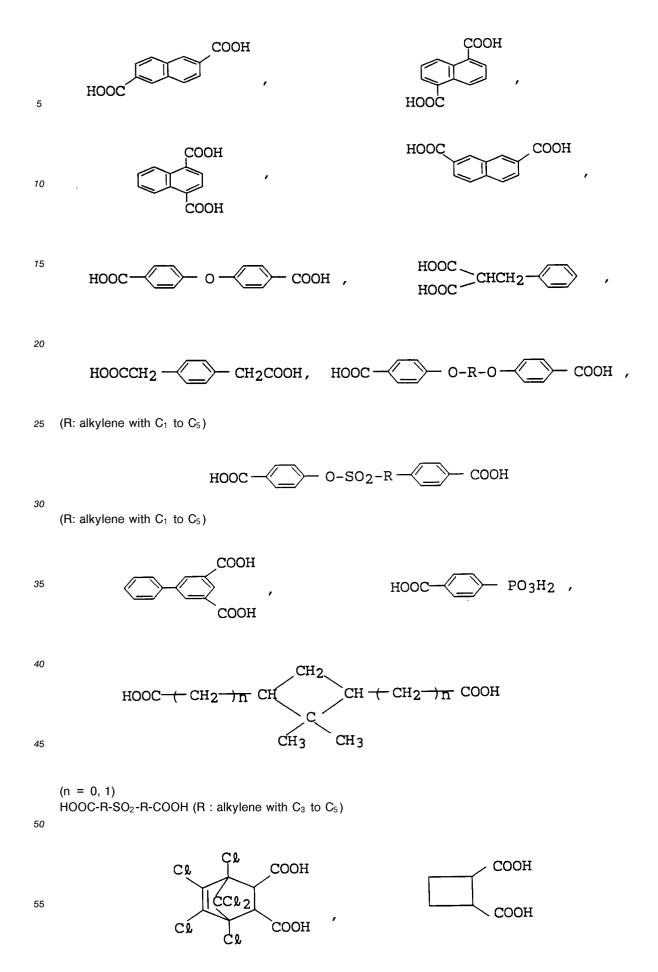


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(X: halogen atom)



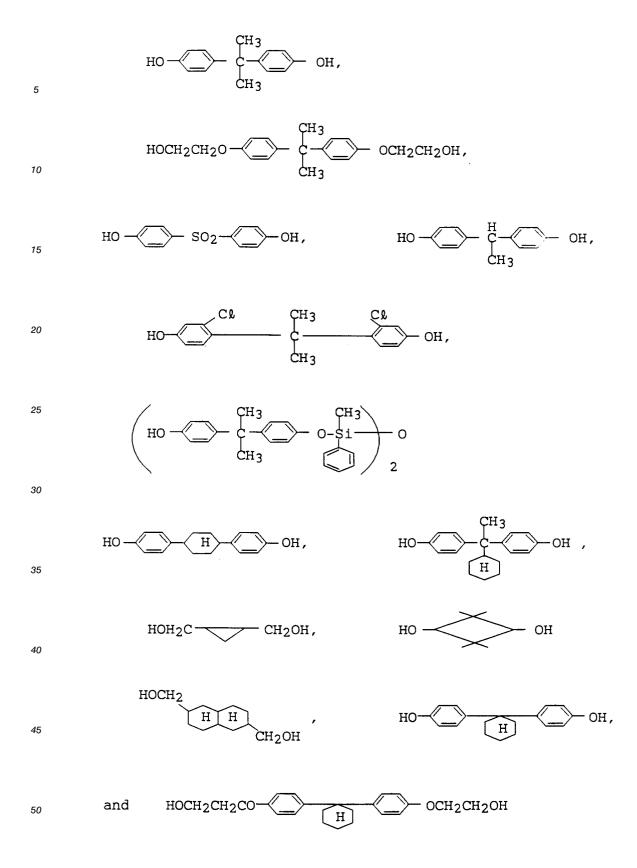
and

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COOH HOOC -

Usable examples of diol are ethyleneglycol, 1,3-propanediol, 1,2-propanediol, 1,4-butanediol, 1,5pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-10 cyclohexanediol, 1,4-cyclohexanedimethanol, 1,3-cyclohexanediol, 1,1-cyclohexanedimethanol, catechol, resorcin, hydroquinone, 1,4-benzenedimethanol,

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In addition, a hydroxyl group-containing compound or an acid-containing compound, which is either 55 mono-functional or polyfunctional (trifunctional or a higher functionality), may be copolymerized as needed. In polyester used in the present invention, a compound having both a hydroxyl group and a carboxyl group (or its ester) in its molecule may be copolymerized. Examples of these compounds are as follows.

HO 
$$\leftarrow$$
 COOH, HOCH<sub>2</sub>CH<sub>2</sub>O  $\leftarrow$  COOCH<sub>3</sub>, CH<sub>3</sub>O CH<sub>3</sub>O HOCH<sub>2</sub>CH<sub>2</sub>O  $\leftarrow$  COOH,

Of the polyesters produced by reacting diol with dicarboxylic acid, more preferable polyesters are homopolymers, such as polyethylene, 2,6-dinaphthalate (PEN), polyacrylate (PAr), and polycyclohex-anedimethanolterephthalate (PCT), and copolymers produced by using 2,6-naphthalenedicarboxylic acid (NDCA), terephthalic acid (TPA), isophthalic acid (IPA), orthophthalic acid (OPA), cyclohexanedicarboxylic acid (CHDC), and paraphenylenedicarboxylic acid (PPDC), as dicarboxylic acid, ethyleneglycol (EG), cyclohexanedimethanol (CHDM), neopentylglycol (NPG), bisphenol A (BPA), and biphenol (BP), as diol, and parahydroxybenzoic acid (PHBA) and 6-hydroxy-2-naphthalenecarboxylic acid (HNCA), as hydroxycarboxylic acid. Of these polyesters, more preferable polyesters are copolymers, such as a copolymer of naphthalenedicarboxylic acid, terephthalic acid, and ethyleneglycol (the mixing molar ratio of naphthalenedicarboxylic acid, terephthalic acid, and ethyleneglycol

- thalenedicarboxylic acid to terephthalic acid is preferably 0.3 : 0.7 to 1.0 : 0, and more preferably 0.5 : 0.5 to 0.8 : 0.2), a copolymer of terephthalic acid, ethyleneglycol, and bisphenol A (the mixing molar ratio of ethyleneglycol to bisphenol A is preferably 0.6 : 0.4 to 0 : 1.0, and more preferably 0.5 : 0.5 to 0.1 : 0.9), a copolymer of isophthalic acid, paraphenylenedicarboxylic acid, terephthalic acid, and ethyleneglycol (the molar ratios of isophthalic acid and paraphenylenedicarboxylic acid assuming that the ratio of terephthalic acid is 1 are preferably 0.1 to 10.0 and 0.1 to 20.0, and more preferably 0.2 to 5.0 and 0.2 to 10.0,
- 30 respectively), a copolymer of naphthalenedicarboxylic acid, neopentylglycol, and ethyleneglycol (the molar ratio of neopentylglycol to ethyleneglycol is preferably 1 : 0 to 0.7 : 0.3, and more preferably 0.9 : 0.1 to 0.6 : 0.4), a copolymer of terephthalic acid, ethyleneglycol, and biphenol (the molar ratio of ethyleneglycol to biphenol is preferably 0 : 1.0 to 0.8 : 0.2, and more preferably 0.1 : 0.9 to 0.7 : 0.3), and a copolymer of parahydroxybenzoic acid, ethyleneglycol, and terephthalic acid (the molar ratio of parahydroxybenzoic acid)
- to ethyleneglycol is preferably 1.0 : 0 to 0.1 : 0.9, and more preferably 0.9 : 0.1 to 0.2 : 0.8). The polyester may also be a polymer blend, such as a polymer blend of PEN and PET (the composition ratio is preferably 0.3 : 0.7 to 1.0 : 0, and more preferably 0.5 : 0.5 to 0.8 : 0.2) and a polymer blend of PET and PAr (the composition ratio is preferably 0.6 : 0.4 to 0 : 1.0, and more preferably 0.5 : 0.5 to 0.1 : 0.9).
- Of the polyesters, PEN is best balanced and has a high dynamic strength, particularly a high elasticity, and a sufficiently high glass transition point of around 120 °C. However, PEN has a drawback of emitting fluorescence. PCT, on the other hand, also has a high dynamic strength and the high glass transition temperature of around 110 °C. The crystallization rate of PCT, however, is very high to make formation of transparent films difficult. PAr has the highest glass transition temperature (190 °C), of the polymers, but has a drawback of a lower dynamic strength than that of PET. To compensate for these drawbacks, therefore, it is preferable to blend these polymers or use a copolymer of monomers forming these
- polymers.

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These homopolymers and copolymers can be synthesized in accordance with known polyester manufacturing methods. As an example, the synthesis can be performed by esterifying an acid component directly with a glycol component, or, when dialkylester is to be used as an acid component, by

- transesterifying the acid component with a glycol component and heating the resultant substance under a reduced pressure to remove an excess glycol component. Alternatively, an acid halide may be used as an acid component and be reacted with glycol. In this case, transesterification, a catalyst, or a polymerization reaction catalyst may be used, or a heat-resistant stabilizer may be added, if necessary. These polyester synthesizing methods can be performed by making reference to, e.g., Polymer Experiments, Vol. 5, "Polycondensation and Polyaddition" (Kyoritsu Shuppan, 1980), pages 103 to 136, and "Synthetic Polymer
  - V" (Asakura Shoten, 1971), pages 187 to 286.

A preferable average molecular weight of these polyesters ranges between about 10,000 and about 500,000.

Polymer blends of the polymers thus obtained can be easily formed in accordance with the methods described in JP-A-49-5482, JP-A-64-4325, JP-A-3-192718, and Research Disclosure Nos. 283,739-41, 284,779-82, and 294,807-14.

Preferable practical examples of a polyester compound for use in the present invention are presented below, but the present invention is not limited to these examples.

Examples of polyester compound

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•	•Homopolymers			
	PEN:	[2,6-naphthalenedicarboxylic acid (NDCA)/ethyleneglycol (EG) (100/100)]	Tg = 119°C	
	PCT:	[terephthalic acid (TPA)/cyclohexanedimethanol (CHDM) (100/100)]	Tg = 93°C	
	PAr:	[TPA/bisphenol A (BPA) (100/100)]	Tg = 192°C	

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<ul> <li>Copolym</li> </ul>	•Copolymers (numbers given in parentheses represent a molar ratio)			
PBC-1	PBC-1 2,6-NDCA/TPA/EG (50/50/100) Tg = 92 °C			
PBC-2	2,6-NDCA/TPA/EG (75/25/100)	Tg = 102°C		
PBC-3	2,6-NDCA/TPA/EG/BPA (50/50/75/25)	Tg = 112°C		
PBC-4	TPA/EG/BPA (100/50/50)	Tg = 105 ° C		
PBC-5	TPA/EG/BPA (100/25/75)	Tg = 135°C		
PBC-6	TPA/EG/CHDM/BPA (100/25/25/50)	Tg = 115°C		
PBC-7	IPA/PPDC/TPA/EG (20/50/30/100)	Tg = 95°C		
PBC-8	NDCA/NPG/EG (100/70/30)	Tg = 105°C		
PBC-9	TPA/EG/BP (100/20/80)	Tg = 115°C		
PBC-10	PHBA/EG/TPA (200/100/100)	Tg = 125°C		

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	•Polymer blends (numbers given in parentheses representa weight ratio)			
Γ	PBB-1	PEN/PET (60/40)	Tg = 95°C	
	PBB-2	PEN/PET (80/20)	Tg = 104°C	
	PBB-3	PAr/PEN (50/50)	Tg = 142°C	
	PBB-4	PAr/PCT (50/50)	Tg = 118°C	
	PBB-5	PAr/PET (60/40)	Tg = 101°C	
	PBB-6	PEN/PET/PAr (50/25/25)	Tg = 108°C	

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Any of the above polyesters has a higher flexural modulus than that of triacetylcellulose, making formation of thin films possible. Of the polyesters, however, PEN has the highest flexural modulus, and hence the use of PEN makes a film thickness of 80  $\mu$ m possible, whereas the film thickness obtained by TAC is 122  $\mu$ m.

- <sup>45</sup> The thickness of these polymer films is preferably 40  $\mu$ m to 300  $\mu$ m. No transparent polymer film with a thickness of 40  $\mu$ m or less can have a flexural modulus high enough to resist the shrinkage stress of a light-sensitive layer. A film thickness of 300  $\mu$ m or more makes the use of a thin spool insignificant. The film thickness is more preferably 40 to 150  $\mu$ m, and most preferably 50 to 120  $\mu$ m.
- An ultraviolet absorbent may be incorporated into these polymer films for the purposes of preventing emission of fluorescence and imparting stability with time. This ultraviolet absorbent preferably has no absorption in a visible region, and the addition amount of the ultraviolet absorbent is normally about 0.5 wt% to 20 wt%, preferably 1 wt% to 10 wt% with respect to the weight of a polymer film. If the addition amount is less than 0.5 wt%, the effect of suppressing degradation in ultraviolet rays cannot be expected. Examples of the ultraviolet absorbent are benzophenone-based ultraviolet absorbents, such as 2,4-dihydrox-
- <sup>55</sup> ybenzophenone, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-n-octoxybenzophenone, 4-dodecyloxy-2hydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, and 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, benzotriazole-based ultraviolet absorbents, such as 2(2'-hydroxy-5'-methylphenyl)benzotriazole, 2(2'-hydroxy-3',5'-di-t-butylphenyl)benzotriazole, and 2(2'-hydroxy-3'-t-butyl-5'-methylphenyl)benzotriazole,

and salicylic acid-based ultraviolet absorbents, such as phenyl salicylate and methyl salicylate.

One of problems arising when a polyester film is used as the support of a photographic light-sensitive material is fogging due to light piping phenomena which occurs because the support has a high refractive index.

The refractive index of polyester, especially aromatic polyester is as high as 1.6 to 1.7, whereas that of 5 gelatin which is a main component of light-sensitive layers coated on the support is low, 1.50 to 1.55. Therefore, light incident from a film edge is easily reflected by the interface between the base and an emulsion layer. As a result, a polyester film brings about a so-called light-piping phenomenon.

As a method of avoiding this light-piping phenomenon, a method of adding inert inorganic grains to a film and a method of adding dyes are known. A light-piping preventing method preferred in the present invention is the method using the addition of dyes, in which a film haze is not increased significantly.

Although dyes for use in film dyeing are not particularly limited, gray dyeing is preferred as a tone when general properties of a light-sensitive material are taken into consideration, and a dye having a high heat resistance within the temperature range of manufacture of polyester films and a high miscibility with polyester is preferred.

In this respect, the above object can be achieved by mixing dyes commercially available as dyes for polyester, such as Diaresin available from Mitshubishi Kasei Corp. or Kayaset available from NIPPON KAYAKU CO. LTD.

As for a dyeing density, a color density in a visible light region must be at least 0.01 or more, more preferably 0.03 or more when measured by a Macbeth color densitometer. 20

The polyester film used in the present invention can be imparted with a lubricating property in accordance with the intended use. Although lubricating property imparting means is not particularly limited, incorporating an inert inorganic compound or coating a surfactant, for example, is used as a general method.

- Examples of such inert inorganic grains are SiO<sub>2</sub>, TiO<sub>2</sub>, BaSO<sub>4</sub>, CaCO<sub>3</sub>, talc, and kaoline. In addition to 25 the above lubricating property imparting method using an external grain system, in which inert grains are added to the polyester synthesis reaction system, it is also possible to adopt a lubricating property imparting method using an internal grain system, in which a catalyst added in a polymerization reaction of polyester is precipitated.
- These lubricating property imparting means are not particularly limited as described above. Since, 30 however, the transparency is an important factor of the support for a photographic light-sensitive material, it is preferable to select, as the external grain system, SiO<sub>2</sub> with a refractive index relatively close to that of a polyester film, or to select the internal grain system capable of decreasing the size of grains to be precipitated.
- In addition, in imparting the lubricating property by means of incorporation, a method of stacking a layer 35 imparted with this property is also preferred in order to obtain a higher transparency of a film. A practical example of this means is a co-extrusion process using a plurality of extruders and a feed block or a multimanifold die.
- When any of these polymer films is used as a support, it is very difficult to strongly adhere photographic layers (e.g., light-sensitive silver halide emulsion layers, interlayers, and filter layers), which 40 consist of protective colloid containing gelatin as its main component to the support because all of these polymer films have hydrophobic surfaces. Conventional techniques attempted to eliminate this problem are the following two methods.

(1) One is a method of performing a surface activating treatment, such as a chemical treatment, a 45 mechanical treatment, a corona discharge treatment, a flame treatment, an ultraviolet treatment, a highfrequency treatment, a glow discharge treatment, an active plasma treatment, a laser treatment, a mixed acid treatment, or an ozone oxidation treatment, and then coating photographic emulsions directly to obtain an adhesive power.

- (2) The other is a method of forming a subbing layer, after performing any of the above surface treatments or without performing any surface treatment, and then coating photographic emulsion layers 50 on this subbing layer (e.g., U.S. Patents 2,698,241, 2,764,520, 2,864,755, 3,462,335, 3,475,193, 3,143,421, 3,501,301, 3,460,944, and 3,674,531, British Patents 788,365, 804,005, and 891,469, JP-B-48-43122 ("JP-B" means Published Examined Japanese Patent Application), and JP-B-51-446).
- Any of these surface treatments more or less forms a polar group on the surface of a support that is originally hydrophobic or increases the crosslinking density of the surface. It is considered that the affinity 55 of the surface for a polar group of a component contained in the subbing solution is increased or the fastness of the bonding surface is increased as a consequence. In addition, various improvements are made for the arrangement of the subbing layers. Examples are a so-called multilayer method, in which a layer (to

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be abbreviated as a first subbing layer hereinafter) which adheres well to a support is formed as a first layer and a hydrophilic resin layer (to be abbreviated as a second subbing layer hereinafter) which adheres well to a photographic layer is formed as a second layer on the first layer, and a single-layer method, in which only one resin layer containing both a hydrophobic group and a hydrophilic group is coated.

<sup>5</sup> Of the surface treatments described in item (1) above, the corona discharge treatment is well known to those skilled in the art and can be achieved by any conventional method, such as those disclosed in JP-B-48-5043, JP-B-47-51905, JP-A-47-28067, JP-A-49-83767, JP-A-51-41770, and JP-A-51-131576. A discharge frequency is 50 Hz to 5,000 kHz, preferably 5 kHz to several hundred kHz. If the discharge frequency is too low, not only no stable discharge can be obtained but pin holes are formed in an object to be treated,

10 leading to an undesirable result. If the discharge frequency is too high, on the other hand, a special apparatus for obtaining impedance matching is required to undesirably increase the cost of an entire system. To improve the wettability of a plastic film such as usual polyester or polyolefin, the treatment intensity for an object to be treated is appropriately 0.001 to 5 KV•A•min/m<sup>2</sup>, preferably 0.01 to 1 KV•A•min/m<sup>2</sup>. A proper gap clearance between an electrode and a dielectric roll is 0.5 to 2.5 mm, preferably 1.0 to 2.0 mm.

The glow discharge treatment which is the most effective surface treatment in many cases can be performed by any conventional method, such as those disclosed in JP-B-35-7578, JP-B-36-10336, JP-B-45-22004, JP-B-45-22005, JP-B-45-24040, JP-B-46-43480, U.S. Patents 3,057,792, 3,057,795, 3,179,482, 3,288,638, 3,309,299, 3,424,735, 3,462,335, 3,475,307, and 3,761,299, British Patent 997,093, and JP-A-53-129262.

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Generally, an appropriate pressure of the glow discharge treatment is 0.005 to 20 Torr, preferably 0.02 to 2 Torr. If the pressure is too low, the surface treating effect is weakened. If the pressure is too high, an overcurrent flows to allow easy occurrence of sparks. These sparks are dangerous and may destroy an object to be treated. Discharge occurs upon application of a high voltage across one or more pairs of metal

25 plates or metal bars spaced apart from each other in a vacuum tank. This voltage can take various values depending on the composition and the pressure of an atmospheric gas. Within the above-mentioned pressure range, however, a stable steady glow discharge occurs at a voltage of 500 to 5,000 V. A voltage particularly suitable for improvement in adhesive power ranges between 2,000 and 4,000 V.

A discharge frequency is appropriately from 0, i.e., DC, to several thousand Hz, preferably 50 Hz to 20 30 MHz, as can be seen in conventional techniques. A discharge treatment intensity is properly 0.01 to 5 kV•A•min/m<sup>2</sup>, preferably 0.15 to 1 kV•A•min/m<sup>2</sup> because a desired adhesive power can be obtained.

The subbing methods of item (2) will be described below. These methods have been studied well in this field of art. As the material of the first subbing layer in the multilayer method, researchers have examined the characteristics of a copolymer formed by using, as its starting material, a monomer selected

<sup>35</sup> from, e.g., vinyl chloride, vinylidene chloride, butadiene, methacrylic acid, acrylic acid, itaconic acid, and maleic anhydride, as well as the characteristics of many polymers, such as polyethyleneimine, an epoxy resin, graft gelatin, and nitrocellulose. As the material of the second subbing layer in the multilayer method, the characteristics primarily of gelatin have been investigated.

In the single-layer method, a high adhesive power is in many cases achieved by swelling a support to 40 cause interfacial mixing with a subbing hydrophilic polymer.

Examples of the subbing hydrophilic polymer usable in the present invention are a water-soluble polymer, cellulose ester, a latex polymer, and water-soluble polyester. Examples of the water-soluble polymer are gelatin, a gelatin derivative, casein, agar-agar, soda alginate, starch, polyvinyl alcohol, a polyacrylic acid copolymer, and a maleic anhydride copolymer. Examples of the cellulose ester are a

45 carboxymethylcellulose and hydroxyethylcellulose. Examples of the latex polymer are a vinyl chloridecontaining copolymer, a vinylidene chloride-containing copolymer, an acrylic ester-containing copolymer, a vinyl acetate-containing copolymer, and a butadiene-containing copolymer. Gelatin is most preferred of the polymers.

Examples of a compound for swelling a support, which can be used in the present invention, are resorcin, chlororesorcin, methylresorcin, o-cresol, m-cresol, p-cresol, phenol, o-chlorophenol, pchlorophenol, dichlorophenol, trichlorophenol, monochloroacetic acid, dichloroacetic acid, trifluoroacetic acid, and chloral hydrate. Of these compounds, resorcin and p-chlorophenol are preferable.

In the present invention, various gelatin hardeners can be used in the subbing layer.

Examples of the gelatin hardener are chromium salt (e.g., chromium alum), aldehydes (e.g., formal-55 dehyde and glutaraldehyde), isocyanates, an active halogen compound (e.g., 2,4-dichloro-6-hydroxy-Striazine), and an epichlorohydrin resin.

In the present invention, the subbing layer can contain fine grains of an inorganic substance, such as  $SiO_2$ ,  $TiO_2$ , or a matting agent, or fine grains (1 to 10  $\mu$ m) of a polymethylmethacrylate copolymer.

In addition to the above substances, the subbing solution may contain various additives as needed. Examples of the additives are a surfactant, an antistatic agent, an antihalation agent, a coloring dye, a pigment, a coating aid, and an antifoggant. In the present invention, when the subbing solution for the first subbing layer is to be used, this subbing solution need not contain any etching agent, such as resorcin, chloral hydrate, or chlorophenol. It is, however, also possible to add such etching agents as needed.

- The subbing solution for use in the present invention can be coated by well-known coating processes, such as a dip coating process, an air knife coating process, a curtain coating process, a roller coating process, a wire bar coating process, a gravure coating process, and the extrusion coating process using a hopper, described in the specification of U.S. Patent 2,681,294. If necessary, it is also possible to coat two or more layers simultaneously in accordance with any of the processes described in the specifications of
- 10 U.S. Patents 2,761,791, 3,508,947, 2,941,898, and 3,526,528 and the process described in Yuji Harazaki, "Coating Engineering," page 253 (published by Asakura Shoten, 1973).

A binder used in the back layer may be either a hydrophobic polymer or a hydrophilic polymer such as used in the subbing layer.

- The back layer of the light-sensitive material of the present invention may contain, e.g., an antistatic 15 agent, a lubricating agent, a matting agent, a surfactant, and a dye. In the present invention, the antistatic agent usable in the back layer is not particularly limited. Examples of an anionic polymer electrolyte as the antistatic agent are polymers containing carboxylic acid, carboxylate, and sulfonate, such as those described in JP-A-48-22017, JP-B-46-24159, JP-A-51-30725, JP-A-51-129216, and JP-A-55-95942. Exam-
- ples of a cationic polymer are described in JP-A-49-121523, JP-A-48-91165, and JP-B-49-24582. The ionic 20 surfactant also involves both anionic and cationic compounds, such as those described in JP-A-49-85826, JP-A-49-33630, U.S. Patents 2,992,108 and 3,206,312, JP-A-48-87826, JP-B-49-11567, JP-B-49-11568, and JP-A-55-70837.
  - The most preferable substance as the antistatic agent used in the back layer of the present invention is a fine grain of at least one crystalline metal oxide selected from ZnO, TiO<sub>3</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, BaO, and MoO<sub>3</sub>, or a fine grain of a composite oxide of these oxides.
  - The fine grains of the conductive crystalline oxides or their composite oxide used in the present invention have a volume resistivity of  $10^7 \Omega \cdot cm$  or less, more preferably  $10^5 \Omega \cdot cm$  or less and a grain size of 0.01 to 0.7  $\mu$ m, most preferably 0.02 to 0.5  $\mu$ m.
- Methods of manufacturing the fine grains of the conductive crystalline metal oxides or their composite 30 oxide used in the present invention are described in detail in JP-A-56-143430 and JP-A-60-258541. Examples of a method that can be performed easily are: 1) a method of forming fine metal oxide grains by calcination and heat-treating the resultant fine grains in the presence of a hetero-atom for improving the conductivity, 2) a method of allowing a hetero-atom for improving the conductivity to be present in the
- manufacture of fine metal oxide grains performed by calcination and 3) a method of reducing an oxygen 35 concentration in an atmosphere to introduce oxygen defects in the manufacture of fine metal oxide grains performed by calcination. Examples of the hetero-atom are At and In, for ZnO, Nb and Ta, for TiO<sub>2</sub>, and Sb, Nb, and a halogen element, for SnO<sub>2</sub>. The addition amount of the hetero-atom is preferably 0.01 to 30 mol%, and most preferably 0.1 to 10 mol%.
- The number of perforations, the imaging area, and the area of the imaging area of a silver halide color 40 photographic light-sensitive material according to the present invention will be described below with reference to the accompanying drawings.

In the silver halide color photographic light-sensitive material of the present invention, perforations are formed in one or both of side edge portions along the longitudinal direction of a roll-like support. It is also possible to form perforations in only one side edge portion and magnetically or optically record information 45 obtained during the manufacture of a light-sensitive material and information concerning the exposure conditions in photographing in the other side edge portion. When perforations are formed in both side edge portions, the above information can be recorded between these perforations.

Practical examples of the construction of such a light-sensitive material are shown in Figs. 1 to 9.

Figs. 1 to 8 are plan views each showing a part of a film according to the present invention, and Fig. 9 50 is a view showing the section in the direction of thickness of the film shown in each of Figs. 1 to 8.

As shown in Figs. 1 to 8, a film is a long belt-like product constituted by imaging areas 1 formed through photographing (exposure) and frame portions 2 and 3 formed on both sides of the imaging areas 1 in the widthwise direction of the film. The frame portions 2 and 3 preferably function as information

recording portions. For example, optical information recording portions or magnetic recording portions 55 consisting of magnetic layers are formed as the frame portions 2 and 3. More specifically, a magnetic recording track 4 can be formed in the frame portion 2 along the longitudinal direction of the film F. As shown in Fig. 9, this magnetic recording track 4 is formed by coating a magnetic material 7 on the surface

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of the film F opposite to the surface on which a hydrophilic colloid layer 8 is formed. The magnetic recording track 4 can also be formed on the same surface as the hydrophilic colloid layer 8. It is also possible to form the magnetic recording track 4 in the frame portion 3 or in the both side edge portions (frame portions 2 and 3). In this magnetic recording track 4, specific information of the film, photographing

- <sup>5</sup> information, and laboratory processing information (these information will be simply referred to as information hereinafter) are magnetically recorded for one film or for each imaging area in the manufacture of the film, in photographing, and in the processing of the film. In this case, the specific information of the film includes the name of the manufacturer, the type of the film, the date of manufacture, and the frame number, the photographing information includes the data of photographing, the use/nonuse of a flash bulb, a shutter
- <sup>10</sup> speed, and an f-number, and the laboratory processing information includes the name of a color laboratory company, the type of color development, the type of a developing machine, the date of processing, the name of a person in charge of processing, and the conditions of exposure for color paper.

To read out the information recorded in the magnetic recording track 4, while the film F is fed in its longitudinal direction, reading means, such as a magnetic head, is brought into contact with the magnetic recording track 4 to extract the information as an electrical signal.

Perforations (holes) 5 for feeding or positioning the film inside, e.g., a camera are formed in the frame portion 3.

The number of the perforations is preferably as small as possible. Although films are fed by using perforations in currently available cameras, perforations can be decreased in number by using a film

- 20 feeding mechanism which does not use perforations so that perforations in a number required to position a film in a camera or a printer need only be formed. The number of perforations is preferably one to four, and most preferably one or two per frame (S<sub>1</sub>). In this case, the frame corresponds to an area A × B in the film shown in Fig. 2.
- In the present invention, the perforations 5 are formed in the frame portion 2 or 3 formed in the side edge portion in the widthwise direction of the film F, as shown in Figs. 1, 2, 4, and 6, or in both of the frame portions 2 and 3, as shown in Figs. 3, 5, 7, and 8.

The shape of the perforations is not particularly limited. For example, the perforations may take rectangular shapes as shown in Figs. 1, 2, and 4, polygonal shapes such as a hexagon (note that the corners of such a polygonal perforation may be formed by curved lines with a certain predetermined radius

30 of curvature), or circular shapes (which may be an ellipse or other deformed circles) as shown in Figs. 3 and 8. When a plurality of perforations are formed for each frame, the shapes of these perforations may be either the same, as shown in Figs. 3, 4, and 8, or different, as shown in Figs. 5, 6, and 7.

Although the size of the perforations is also not particularly limited, smaller perforations are preferred in order for the frame portions 2 and 3 described above to function as the information recording portions. The ratio of the total area of perforations is 5% or less, preferably 3% or less, and most preferably 0.1% to 2%

with respect to the area of one frame (A  $\times$  B = S<sub>1</sub> in Fig. 2).

In the present invention, to keep the area of the optical or magnetic information recording portion, an area of an imaging area (an exposure portion in the frame) is set to 3 to 7 cm<sup>2</sup>, most preferably 4.0 to 6.0 cm<sup>2</sup>.

40 The length of the long belt-like film F is 200 cm or less, preferably 180 cm or less, and most preferably 165 cm or less. The lower limit of the length of the film F is 40 cm. The width of the film F is 35 mm or less, preferably 10 to 32 mm, and most preferably 15 to 30 mm.

As a result of extensive studies, on the other hand, it is found that variations of the compositions of pictures are greatly increased in number if prints with the following three aspect ratios (the lateral length/longitudinal length ratio of an imaging area) can be provided. The three aspect ratios are as follows.

(1) Low aspect ratio	1.40 to 1.60
(2) Middle aspect ratio	1.70 to 1.90
(3) High aspect ratio	2.00 to 3.00

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It is, of course, also possible to further increase the types of prints.

When the aspect ratio (b/a ratio in Fig. 2) of the imaging area of the color negative film is set at the middle aspect ratio of item (2) above, the enlargement ratio of a panoramic print (high-aspect-ratio print) can be decreased compared to those in conventional products, thereby improving the image quality of the print. In the present invention, therefore, the aspect ratio of the imaging area of the color negative film is set between preferably 1.40 and 2.50, more preferably 1.60 and 2.20, and furthermore preferably 1.70 and 1.90.

It is preferable to set the aspect ratio at a value close to the aspect ratio (1.78) of an HDTV because hybridization of a silver salt photographic system and an electronic imaging system can be advanced smoothly. That is, the most preferable aspect ratio is 1.75 to 1.85.

- When, on the other hand, the fact that the enlargement ratio increases with the increase in aspect ratio of a print is taken into account, the area of one imaging area is desirably 3.0 cm<sup>2</sup> or more in order to maintain the image quality of the print. If, however, the area exceeds that of an imaging area of a current 135-size film, the dimensions of a magazine or a camera are undesirably increased. Therefore, the desirable area of one imaging area is 3.0 to 8.6 cm<sup>2</sup>.
- As described above, the upper limit of the area of an imaging area is preferably as low as possible in order to keep the area of the optical or magnetic information recording portion, and this is also preferable in miniaturizing a magazine for containing the film. It is, however, difficult to bring about the effects of the present invention to thereby achieve the object of the invention if the area of an imaging area is reduced to one-half or less of the current size. For this reason, the area of an imaging area is preferably set between 3.0 and 7.0 cm<sup>2</sup>, most preferably 4.0 and 6.0 cm<sup>2</sup>.
- In addition, in order to keep the area of the optical or magnetic information recording portion, the ratio  $(S_2/S_1)$  of the area  $(S_2)$  of the imaging area  $(a \times b)$  to the area  $(S_1)$  of one frame  $(A \times B)$  is preferably 0.25 to 0.90. To decrease the area of the imaging area or miniaturize a magazine or a camera, the  $S_2/S_1$  ratio is preferably 0.50 to 0.90, more preferably 0.60 to 0.80, and most preferably 0.65 to 0.75.

The above light-sensitive material using the polyester support according to the present invention is preferably used as a color photographic light-sensitive material for photographing, and most preferably color negative photographic light-sensitive material for photographing.

Note that maintaining the flatness of a film during photographing becomes important as the area of the imaging area is decreased to that of a small format, 3.0 to 7.0 cm<sup>2</sup>. Degradation in flatness leads to a focusing failure. In particular, since the enlargement ratio is increased in printing from a small-format film,

the degradation in flatness of a film largely interferes with the expression of sharpness that a color negative light-sensitive material for photographing has. Therefore, it is most preferable to use a light-shielded cartridge which has an attitude control mechanism and can prevent light fog, such as disclosed in JP-A-3-089341, and a camera matching this cartridge.

It is also possible to perform photographing by varying an aspect ratio within the range of 1.40 to 2.50 while the area of the imaging area is kept between 3.0 to 7.0 cm<sup>2</sup>. For example, means or a mechanism described in Japanese Utility Model Application No. 3-072779 can be incorporated into a photographing color light-sensitive material or a camera.

A compound represented by Formula (A) used in the present invention will be described below:

35 Formula (A) A-(Time)<sub>n</sub>-W

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wherein A represents a group capable of releasing  $(Time)_n$ -W upon reacting with the oxidized form of a color developing agent, Time represents a-timing group, W represents a group which exhibits a development inhibiting effect after released from  $(Time)_n$ -W, and n represents an integer of 1, 2, or 3.

Examples of W are a tetrazolylthio group, a thiadiazolylthio group, an oxadiazolylthio group, a triazolylthio group, a benzimidazolylthio group, a benzotriazolylthio group, a tetrazolylseleno group, a benzotriazolyl group, a triazolyl group, a benzoindazolyl group, and derivatives of these groups. These groups are described in, e.g., U.S. Patents 3,227,554, 3,384,657, 3,615,506, 3,617,291, 3,733,201, 3,933,500, 3,958,993, 3,961,959, 4,149,886, 4,259,437, 4,095,984, and 4,477,563, British Patent 1,450,479, and Research Disclosure Vol. 176, No. 17643, (December, 1978).

Examples of Time are a group which uses cleavage of hemiacetal, described in U.S. Patent 4,146,396, 4,652,516, or 4,698,297; a timing group which causes cleavage by using an intramolecular nucleophilic reaction, described in U.S. Patent 4,248,962; a timing group which causes cleavage by using electron transfer, described in U.S. Patent 4,409,323 or 4,421,845; a group which causes hydrolysis of iminoketal,

50 described in U.S. Patent 4,546,073; and a group which causes cleavage by using hydrolysis of ester, described in DE-OS 2,626,317. Time binds to A at a hetero atom, preferably an oxygen atom, a sulfur atom, or a nitrogen atom contained in it.

Preferable examples of Time are a methyleneoxy group, a 4-methylene-3-pyrazolyloxy group, a 2(or 4)methylenephenoxy group, a 2-carbonylaminomethylphenoxy group, a carboxyl group, and a carbomethoxy group.

If n is 2 or 3, a plurality of Time's may be the same or different.

In Formula (A), A specifically represents a coupler moiety.

Examples of the coupler moiety represented by A are a yellow coupler moiety (e.g., an open-chain ketomethylene type coupler moiety, such as acylacetanilide or malondianilide), a magenta coupler moiety (e.g., a 5-pyrazolone type, pyrazolotriazole type, or pyrazoloimidazole type coupler moiety), a cyan coupler moiety (e.g., a phenol type or naphthol type coupler moiety or an imidazole type coupler moiety described

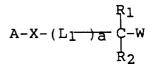
<sup>5</sup> in Published Unexamined European Patent 249,453), and a colorless compound forming coupler moiety (e.g., an indanone type or acetophenone type coupler moiety). The coupler moiety represented by A can also be a heterocyclic coupler moiety described in U.S. Patent 4,315,070, 4,183,752, 4,174,969, 3,961,959, or 4,171,223.

A compound represented by Formula (A) for use in the present invention will be described in more detail below.

A compound represented by Formula (A) is preferably a compound represented by Formula (A1) below:

## Formula (A1)

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In Formula (A1), A and W represent the same meanings as those of A and W in a compound represented by Formula (A).

X represents an oxygen atom, a sulfur atom, or a substituted imino group. It is preferred that the substituent of X combine with  $L_1$  to form a 5- to 7-membered nitrogen-containing heterocyclic ring (which may have a substituent or may be a condensed ring) together with a nitrogen atom of the imino group.

Each of R<sub>1</sub> and R<sub>2</sub> represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, benzyl, dodecyl, and cyclohexyl) with 1 to 36 carbon atoms or an aryl group (e.g., phenyl, 4-methoxyphenyl, 4-chlorophenyl, 4-nitrophenyl, and naphthyl) with 6 to 36 carbon atoms.

 $L_1$  represents a linking group in which W cleaves from a moiety [-C(R<sub>1</sub>)(R<sub>2</sub>)-W] on the right of L<sub>1</sub> through electron transfer after a bond on the left of L<sub>1</sub> cleaves in a compound represented by Formula (A1). a represents 0, 1, or 2. If a represents 2, two L<sub>1</sub>'s may be the same or different.

Of the compounds represented by Formula (A1), compounds represented by Formulas (A-I) to (A-IV) below are more preferable:

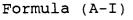
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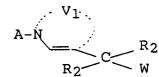
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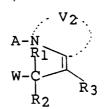
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Formula (A-II)



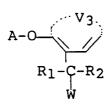
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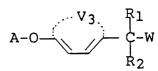
Formula (A-III)



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Formula (A-IV)

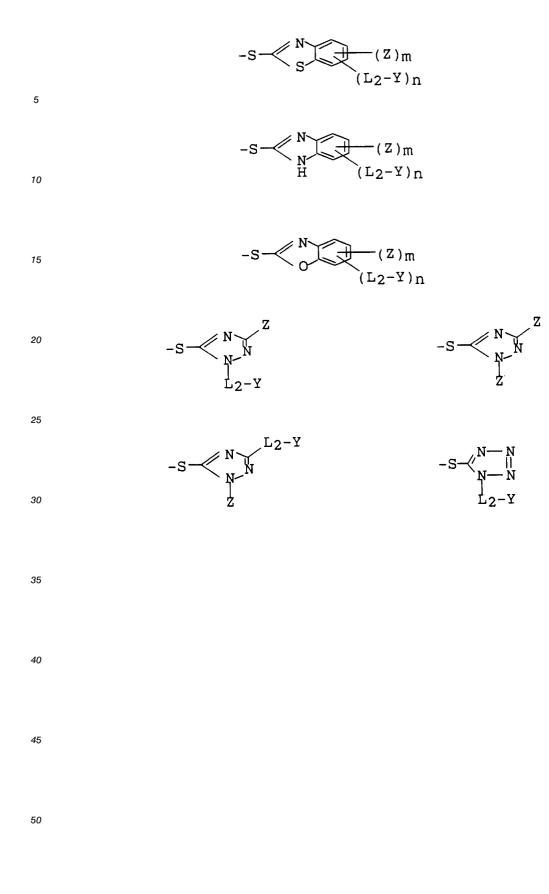


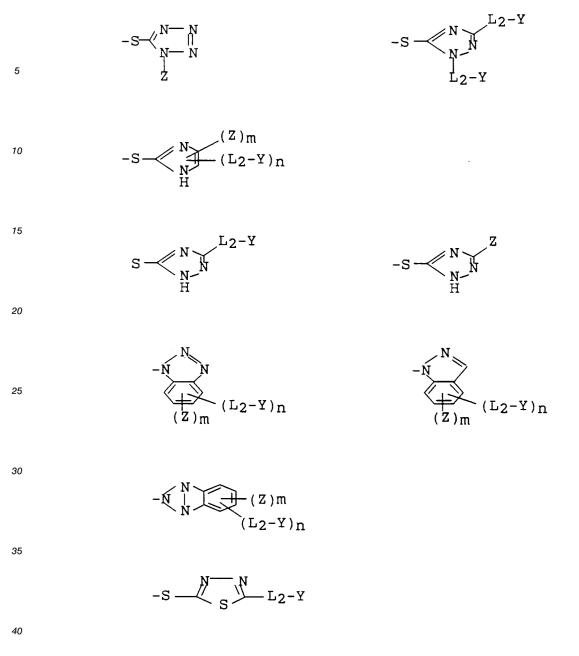
In the above formula, each of V<sub>1</sub> and V<sub>2</sub> represents a nonmetallic atomic group required to form a 5- to 7-membered nitrogen-containing heterocyclic ring (which may have a substituent or may be a condensed ring) together with an atomic group to which it binds, V<sub>3</sub> represents a nonmetallic atomic group required to form a 5- to 7-membered heterocyclic ring (which may have a substituent or may be a condensed ring) or a benzene ring (which may have a substituent or may be a condensed ring) together with an atomic group to which it binds, and R<sub>3</sub> represents a hydrogen atom or a monovalent group. R<sub>3</sub> may combine with V<sub>2</sub> to form a ring.

A basic portion of the development inhibitor represented by W is the heterocyclic group or the heterocyclic thio group enumerated above in the description of Formula (A). Examples are as follows.

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In the above formulas, a substituent (contained in the portion of W in Formula (A)) represented by Z represents a hydrogen atom, a halogen atom, an alkyl group, an alkenyl group, an alkaneamide group, an alkeneamide group, an alkeneamide group, an alkenyl group, an aryl group, or a heterocyclic group, and  $L_2$  includes a chemical bond which cleaves in a developing solution. This chemical bond involves examples listed in Table 1 below. These chemical bonds are cleaved by a nucleophilic reagent such as hydroxylamine or hydroxy ion as a component of a color developing solution.

Chemical bond contained in $L_2$	Cleavage reaction of bond shown in left column (reaction with ©OH)
-COO-	-COOH+HO-
H -NCOO-	-NH2+HO-
-S020-	-SO3H+HO-
-OCH2CH2SO2-	-OH+CH2=CHSO2-
-0C0- ॥ 0	-ОН+НО-
NHCCO-       00	-NH2+HO-

Table 1

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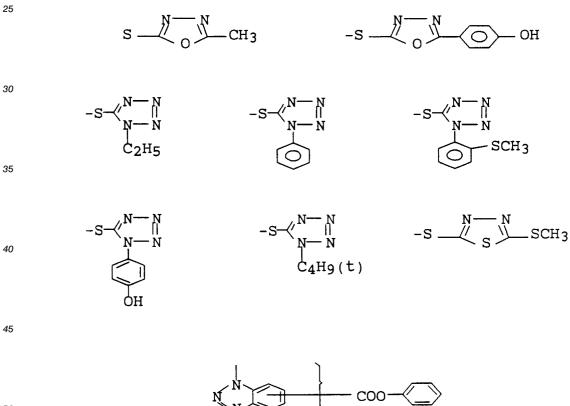
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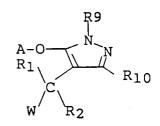
Each of m and n represents an integer of 0 to 4. The development inhibiting component represented by W is most preferably the following compound.



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Of the compounds represented by Formulas (A-I) to (A-IV) above, a compound represented by Formula (A-I) is most preferred, and, of the compounds represented by Formula (A-I), a compound represented by Formula (A-V) below is preferable. 55

Formula (A-V)



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In Formula (A-V), A, R<sub>1</sub>, R<sub>2</sub>, and W have the same meanings as those of A, R<sub>1</sub>, R<sub>2</sub>, and W in Formula (A1) above,  $R_9$  represents an alkyl group (e.g., methyl, benzyl, and dodecyl) with 1 to 24 carbon atoms or an aryl group (e.g., phenyl, 4-tetradecyloxyphenyl, 4-methoxyphenyl, 4-chlorophenyl, 2,5-dichlorophenyl, 4methylphenyl, and 4-nitrophenyl) with 6 to 36 carbon atoms, and R10 represents a hydrogen atom, an alkyl 15 group (e.g., methyl, ethyl, undecyl) with 1 to 24 carbon atoms, an aryl group (e.g., phenyl and 4methoxyphenyl) with 8 to 36 carbon atoms, an alkoxy group (e.g., methoxy, ethoxy, and dodecyloxy) with 1 to 24 carbon atoms, a cyano group, an amino group (e.g., amino, dimethylamino, piperidino, dihexylamino, and anilino) with 0 to 36 carbon atoms, a carbonamide group (e.g., acetamide, benzamide, and tetradecaneamide) with 1 to 24 carbon atoms, a sulfonamide group (e.g., methylsulfonamide and phenylsul-20 fonamide) with 1 to 24 carbon atoms, a carboxy group, an alkoxycarbonyl group (e.g., methoxycarbonyl and dodecyloxycarbonyl) with 2 to 24 carbon atoms, or a carbamoyl group (e.g., carbamoyl, dimethylcarbamoyl, and pyrrolidinocarbamoyl) with 1 to 24 carbon atoms. A in Formula (A-V) is preferably a cyan dye forming coupler moiety (e.g., a phenol-based cyan coupler moiety or an  $\alpha$ -naphthol-based cyan coupler moiety). A is most preferably a coupler moiety which flows out into a processing solution during color development as 25 described in The Journal of The Japan Photographic Society Vol. 52 (1989), No. 2, pages 150 to 155 (Kida

preferably a hydrogen atom, R<sub>9</sub> is preferably an aryl group, and R<sub>10</sub> is preferably an alkyl group. Practical examples of a compound represented by Formula (A) are presented below, but the present invention is not limited to these examples.

et al.), or a coupler moiety the dye formed from which loses its color when bleached. Each of  $R_1$  and  $R_2$  is

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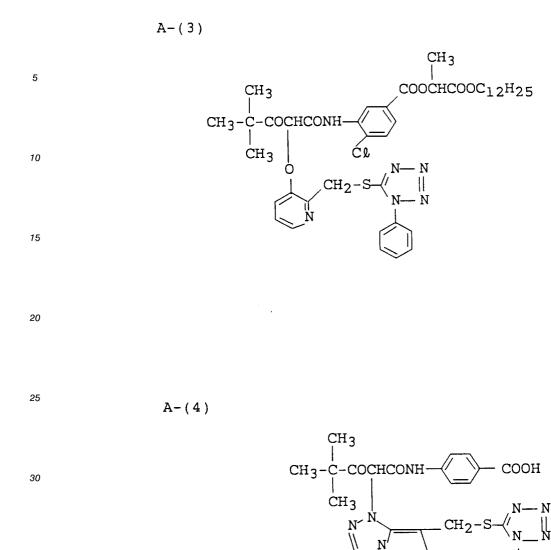
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A-(1) 5 NHCO(CH<sub>2</sub>)<sub>3</sub>O  $C_{5H_{11}}(t)$ CH3 CH<sub>3</sub>-Ċ-COCHCONHćı ĊH3 10 N < N---- N || --- N N-CH2-S-15 N-20 25 A-(2)  $\sum_{C_5H_{11}(t)}^{C_5H_{11}(t)}$ NHCO(CH<sub>2</sub>)<sub>3</sub>0— СH3 30 CH<sub>3</sub>-C-COCHCONH-Ćl Ν 35 CH2-S-⟨<sup>N— N</sup> || N— N 40  $\dot{C}_{4}H_{9}(t)$ 

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 $C_{15}H_{31}CONH$ 



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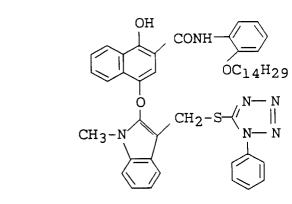
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CH3

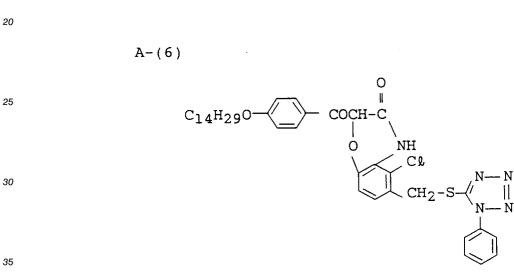
N

A-(5)

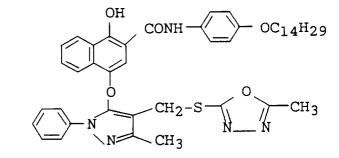




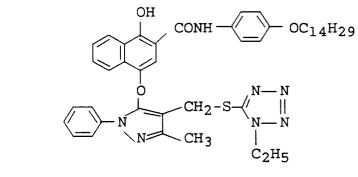




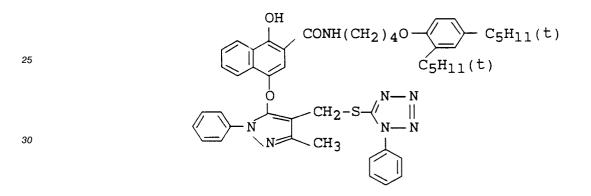




A-(8)



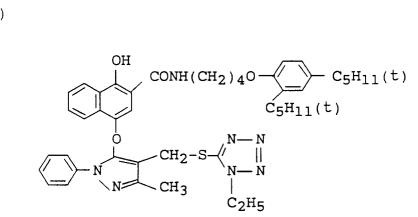
A-(9) 



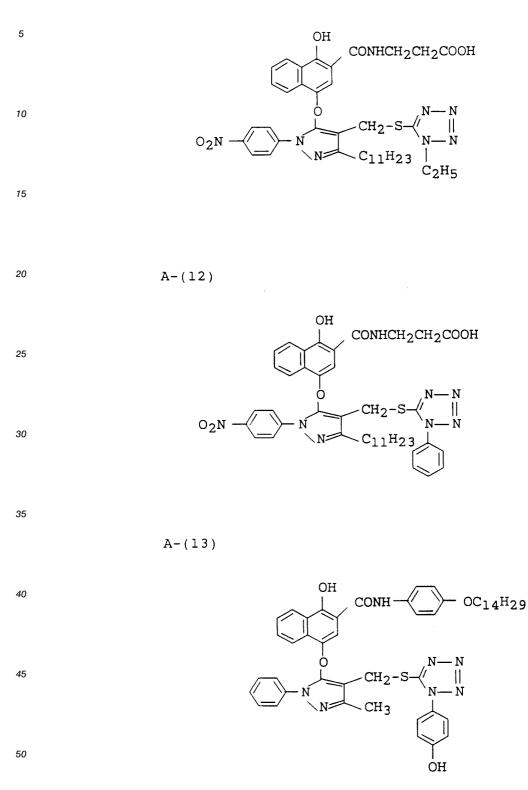
A-(10)



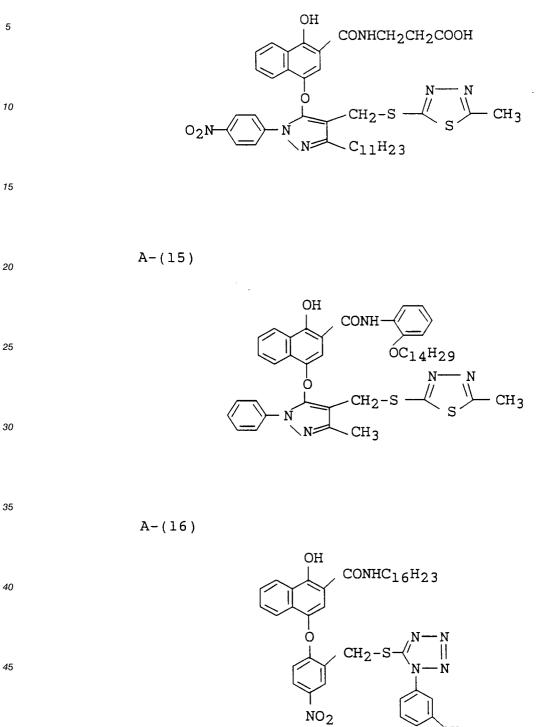




A-(11)



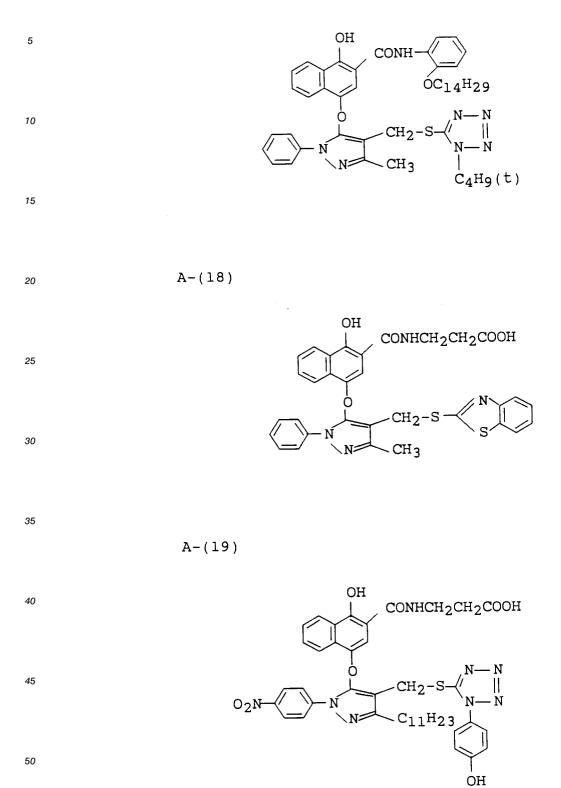
A-(14)



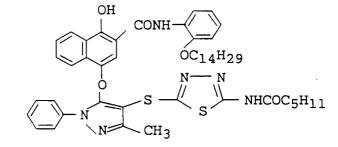
ОН

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A-(17)

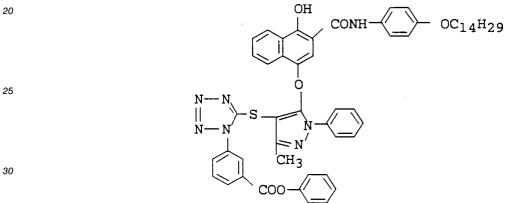


A-(20)

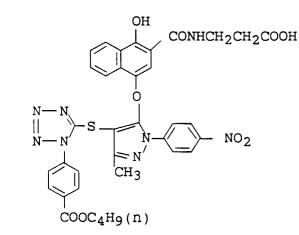


A-(21)

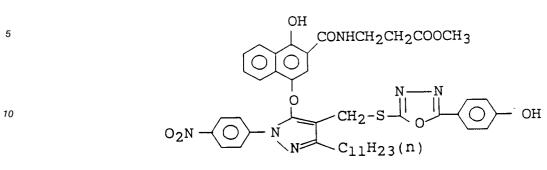


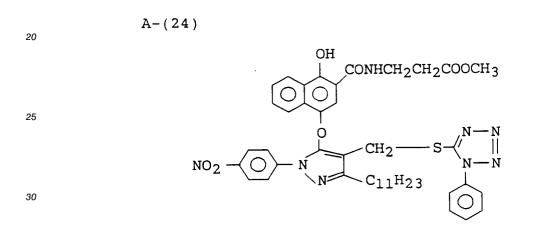


A-(22)



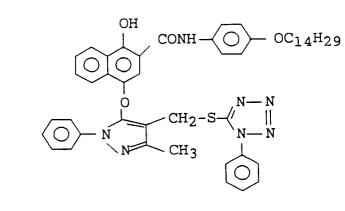
A-(23)

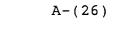


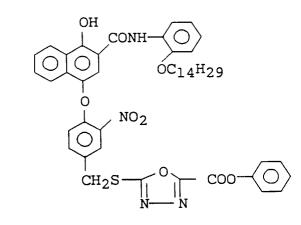


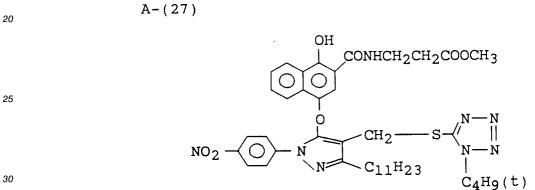


A-(25)

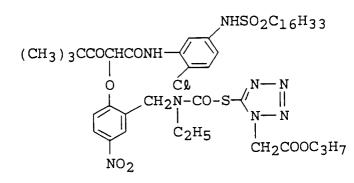




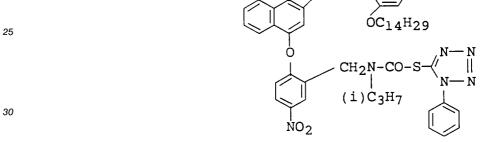






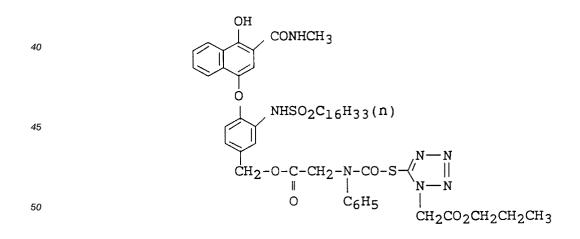


A-(29) NHSO<sub>2</sub>C<sub>16</sub>H<sub>33</sub> 5 (CH<sub>3</sub>) <sub>3</sub>CCOCHCONH Ć٤ Q CH3 и— и || и— и | 10 - CH2-S-NCOO CH<sub>3</sub>Ó NO2 15 A-(30) 20 OH CONH-25

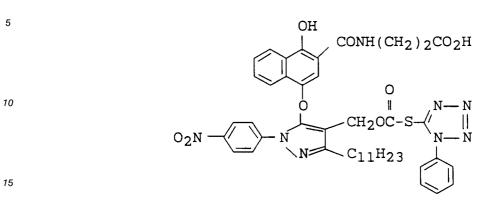


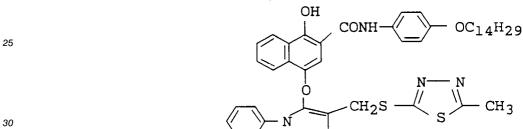
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A-(31)



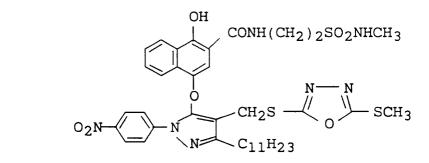
A-(32)





$$\bigwedge_{N} \bigvee_{N} \bigvee_{CH_3} \bigvee_{CH_3} \bigvee_{S} \bigvee_{N} \bigvee_{CH_3} \bigvee_{S} \bigvee_{N} \bigvee_{CH_3} \bigvee_{S} \bigvee_{N} \bigvee_{S} \bigvee_{S$$

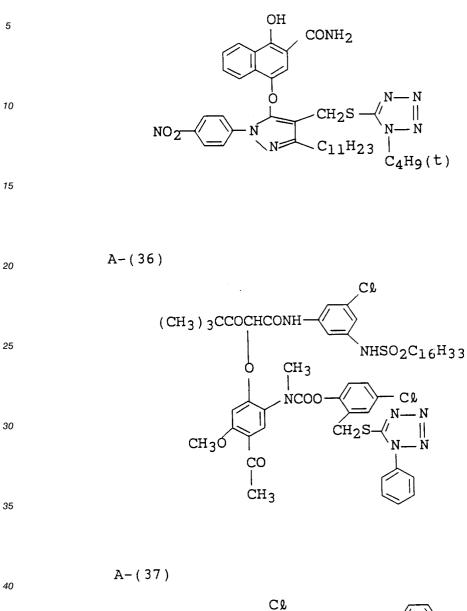
A-(34)

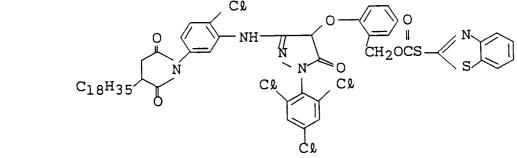


N || N

- N || N

A-(35)

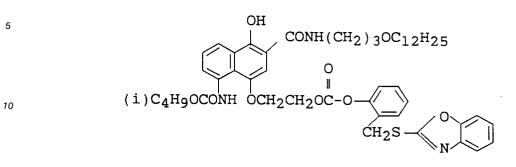




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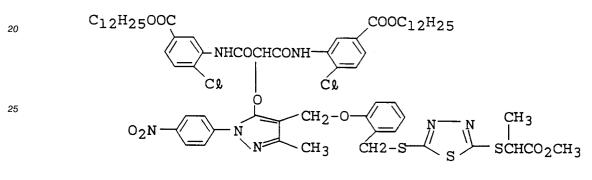
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A-(38)



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A-(39)



OH

Y o I

CH<sub>2</sub>-S

CONH

NO<sub>2</sub>

- N || - N

CH2 -

OCH<sub>3</sub>

 $OC_{14}H_{29}(n)$ 

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A-(40)

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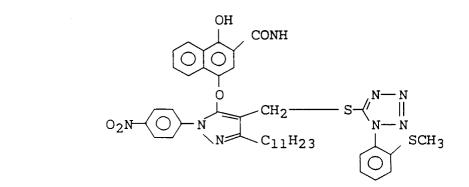
A-(41)  $CC_{14}H_{29}(n)$   $OC_{14}H_{29}(n)$   $OC_{14}H_{29}(n)$  $OC_{14}H_{29}(n)$ 

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A-(42)



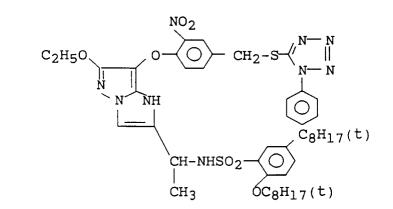
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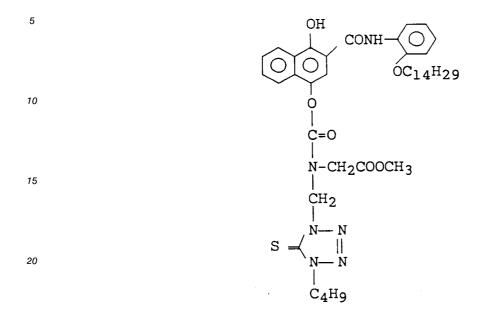
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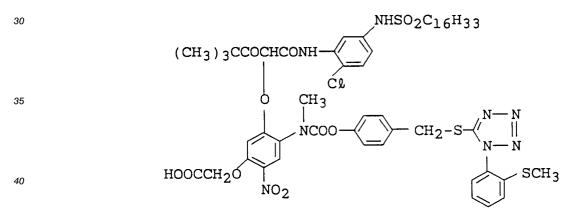
A-(43)



A-(44)



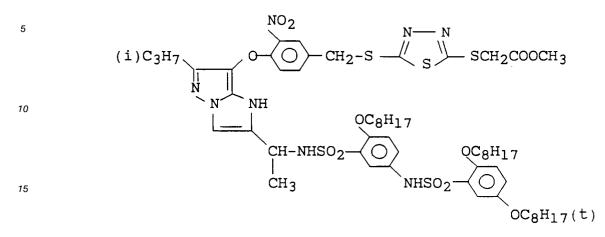
A-(45)



A-(46) CO<sub>2</sub>C<sub>12</sub>H<sub>25</sub> 5 - COCHCONH-| 0 | C=0 | 0 СН30ćı 10 N-N N N CH2S -CH3 CH3 N= 15 20 A-(47) CH3COCHCONH-CO<sub>2</sub>H 25 CH3 0 - N-COO-CH2S-CH3 Ć٤ SO2NHC18H37 30 35 A-(48) OO III CH<sub>3</sub>CCHCNH-CO<sub>2</sub>H 40 ò CH3 CL - N || - N N-COO-45 CH2S SO<sub>2</sub>C<sub>12</sub>H<sub>25</sub>

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- The above compounds which may be used in the present invention can be synthesized easily by the methods described in U.S. Patents 3,227,554, 3,617,291, 3,933,500, 3,958,993, 4,149,886, and 4,234,678, JP-A-51-13239, JP-A-57-56837, U.S. Patents 2,070,266 and 2,072,363, Research Disclosure No. 21228 (December, 1981), JP-B-58-9942, JP-B-51-16141, JP-A-52-90932, U.S. Patent 4,248,962, JP-A-56-114946, JP-A-57-154234, JP-A-58-98728, JP-A-58-209736, JP-A-58-209737, JP-A-58-209738, JP-A-58-209740, JP-25
   A-61-156043, JP-A-61-255342, and JP-A-62-24252.
  - In the present invention, the timing DIR compound represented by Formula (A) is contained in at least one of hydrophilic colloid layers.

In the present invention, the hydrophilic colloid layers involve layers except the support, the back layer, and the subbing layer described above, i.e., involve both light-sensitive layers and non-light-sensitive layers (e.g., an antihalation layer, interlayers, a yellow filter layer, and protective layers) formed on the surface to be exposed of the support. In the present invention, therefore, the timing DIR compound represented by Formula (A) is contained in at least one of these light-sensitive layers and non-light-sensitive layers.

When the timing DIR compound is added to a light-sensitive silver halide emulsion layer, the addition amount is 0.01 to 20 mol%, preferably 0.05 to 10 mol%, and more preferably 0.1 to 5 mol% with respect to the amount of a silver halide in that layer.

When the timing DIR compound is added to a non-light-sensitive layer, the addition amount is 0.01 to 20 mol%, preferably 0.05 to 10 mol%, and more preferably 0.1 to 5 mol% with respect to the amount of a silver halide in a silver halide emulsion layer closest to that non-light-sensitive layer.

- The timing DIR compound represented by Formula (A) can be used singly in two or more layers, or two or more types of these compounds can be used together. It is also possible to use this timing DIR compound in combination with known DIR compounds. When the timing DIR compound of the present invention is to be used in combination with known DIR compounds, a given mixing ratio can be taken in accordance with the performance that the light-sensitive material is required to have.
- The timing DIR compound represented by Formula (A) is used in hydrophilic colloid layers, and is preferably used in a light-sensitive silver halide emulsion layer and/or a layer adjacent to that emulsion layer.

Current photographing color light-sensitive materials are so designed as to achieve the best image quality when enlarged from the size of a 135-format imaging area into a print (8 cm  $\times$  12 cm) of a service size. Therefore, the DIR compound is selected and its addition amount is determined from this viewpoint.

50 When the area of the imaging area of a photographing color light-sensitive material is decreased to that of a small format, the ratio of enlargement into a color print is increased, and this requires further improvements in image qualities, particularly sharpness of the photographing color light-sensitive material. The timing DIR compound represented by Formula A has a startling effect of improving the image qualities.

The silver halide color photographic light-sensitive material (to be abbreviated simply as a light-sensitive material hereinafter) of the present invention will be described in more detail below.

The light-sensitive material of the present invention needs only to have at least one of silver halide emulsion layers, i.e., a blue-sensitive layer, a green-sensitive layer, and a red-sensitive layer, formed on a support. The number or order of the silver halide emulsion layers and the non-light-sensitive layers are

particularly not limited. A typical example is a silver halide photographic light-sensitive material having, on a support, at least one unit light-sensitive layer constituted by a plurality of silver halide emulsion layers which are sensitive to essentially the same color but have different sensitivities or speeds. The unit light-sensitive layer is sensitive to blue, green or red light. In a multi-layered silver halide color photographic light-sensitive

5 material, the unit light-sensitive layers are generally arranged such that red-, green-, and blue-sensitive layers are formed from a support side in the order named. However, this order may be reversed or a layer having a different color sensitivity may be sandwiched between layers having the same color sensitivity in accordance with the application.

Non-light-sensitive layers such as various types of interlayers may be formed between the silver halide 10 light-sensitive layers and as the uppermost layer and the lowermost layer.

The interlayer may contain, e.g., couplers and DIR compounds as described in JP-A-61-43748, JP-A-59-113438, JP-A-59-113440, JP-A-61-20037, and JP-A-61-20038 or a color mixing inhibitor which is normally used.

- As a plurality of silver halide emulsion layers constituting each unit light-sensitive layer, a two-layered 15 structure of high- and low-speed emulsion layers can be preferably used as described in West German Patent 1,121,470 or British Patent 923,045. In this case, layers are preferably arranged such that the sensitivity or speed is sequentially decreased toward a support, and a non-light-sensitive layer may be formed between the silver halide emulsion layers. In addition, as described in JP-A-57-112751, JP-A-62-200350, JP-A-62-206541, and JP-A-62-206543, layers may be arranged such that a low-speed emulsion layer is formed remotely from a support and a high-speed layer is formed close to the support.
  - More specifically, layers may be arranged from the farthest side from a support in an order of lowspeed blue-sensitive layer (BL)/high-speed blue-sensitive layer (BH)/high-speed green-sensitive layer (GH)-/low-speed green-sensitive layer (GL)/high-speed red-sensitive layer (RH)/low-speed red-sensitive layer (RL), an order of BH/BL/GL/GH/ RH/RL, or an order of BH/BL/GL/RL/RH.
- In addition, as described in JP-B-55-34932, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GH/RH/GL/RL. Furthermore, as described in JP-A-56-25738 and JP-A-62-63936, layers may be arranged from the farthest side from a support in an order of blue-sensitive layer/GL/RL/GH/RH.

As described in JP-B-49-15495, three layers may be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an intermediate layer, and a silver halide emulsion layer having sensitivity lower than that of the intermediate layer is arranged as a lower layer. In other words, three layers having different sensitivities may be arranged such that the sensitivity is sequentially decreased toward the support. When a layer structure is constituted by three layers having different sensitivities or

35 speeds, these layers may be arranged in an order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer having the same color sensitivity as described in JP-A-59-202464.

Also, an order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer, or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer may be adopted. Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

To improve the color reproduction, a donor layer (CL) of an interlayer effect can be arranged directly adjacent to, or close to, a main light-sensitive layer such as BL, GL or RL. The donor layer has a spectral sensitivity distribution which is different from that of the main light-sensitive layer. Donor layers of this type are disclosed in U.S. Patent 4,663,271, U.S. Patent 4,705,744, U.S. Patent 4,707,436, JP-A-62-160448, and

## JP-A-63-89850.

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As described above, various layer configurations and arrangements can be selected in accordance with the application of the light-sensitive material.

A preferable silver halide contained in photographic emulsion layers of the photographic light-sensitive material of the present invention is silver bromoiodide, silver chloroiodide, or silver chlorobromoiodide containing about 30 mol% or less of silver iodide. The most preferable silver halide is silver bromoiodide or silver chlorobromoiodide containing about 2 mol% to about 10 mol% of silver iodide.

Silver halide grains contained in the photographic emulsion may have regular crystals such as cubic, octahedral, or tetradecahedral crystals, irregular crystals such as spherical, or tabular crystals, crystals having defects such as twin planes, or composite shapes thereof.

The silver halide may consist of fine grains having a grain size of about 0.2  $\mu$ m or less or large grains having a projected-area diameter of up to 10  $\mu$ m, and the emulsion may be either a polydisperse emulsion or a monodisperse emulsion.

The silver halide photographic emulsion which can be used in the present invention can be prepared by methods described in, for example, Research Disclosure (RD) No. 17643 (December 1978), pp. 22 to 23, "I. Emulsion preparation and types", RD No. 18716 (November 1979), page 648, and RD No. 307105 (November 1989), pp. 863 to 865; P. Glafkides, "Chemie et Phisique Photographique", Paul Montel, 1967;

5 G.F. Duffin, "Photographic Emulsion Chemistry", Focal Press, 1966; and V.L. Zelikman et al., "Making and Coating Photographic Emulsion", Focal Press, 1964.

Monodisperse emulsions described in, for example, U.S. Patents 3,574,628 and 3,655,394, and British Patent 1,413,748 are also preferred.

Also, tabular grains having an aspect ratio of about 3 or more can be used in the present invention. The tabular grains can be easily prepared by methods described in, e.g., Gutoff, "Photographic Science and Engineering", Vol. 14, PP. 248 to 257 (1970); U.S. Patents 4,434,226; 4,414,310; 4,433,048 and 4,499,520, and British Patent 2,112,157.

The crystal structure may be uniform, may have different halogen compositions in the interior and the surface thereof, or may be a layered structure. Alternatively, silver halides having different compositions may be joined by an epitaxial junction, or a compound other than a silver halide such as silver rhodanide or zinc oxide may be joined. A mixture of grains having various types of crystal shapes may be used.

The above emulsion may be of any of a surface latent image type in which a latent image is mainly formed on the surface of each grain, an internal latent image type in which a latent image is formed in the interior of each grain, and a type in which a latent image is formed on the surface and in the interior of each

- 20 grain. However, the emulsion must be of a negative type. When the emulsion is of an internal latent image type, it may be a core/shell internal latent image type emulsion described in JP-A-63-264740. A method of preparing this core/shell internal latent image type emulsion is described in JP-A-59-133542. Although the thickness of a shell of this emulsion changes in accordance with development or the like, it is preferably 3 to 40 nm, and most preferably, 5 to 20 nm.
- A silver halide emulsion layer is normally subjected to physical ripening, chemical ripening, and spectral sensitization steps before it is used. Additives for use in these steps are described in RD Nos. 17,643; 18,716 and 307,105 and they are summarized in the table represented later.

In the light-sensitive material of the present invention, two or more types of emulsions different in at least one of features such as a grain size, a grain size distribution, a halogen composition, a grain shape, and sensitivity can be mixed and used in the same layer.

Surface-fogged silver halide grains described in U.S. Patent 4,082,553, internally fogged silver halide grains described in U.S. Patent 4,626,498 or JP-A-59-214852, and colloidal silver can be preferably used in a light-sensitive silver halide emulsion layer and/or a substantially non-light-sensitive hydrophilic colloid layer. The internally fogged or surface-fogged silver halide grains are silver halide grains which can be uniformly (non-imagewise) developed deprite the presence of a non-expected partient and expected parties.

uniformly (non-imagewise) developed despite the presence of a non-exposed portion and exposed portion of the light-sensitive material. A method of preparing the internally fogged or surface-fogged silver halide grain is described in U.S. Patent 4,626,498 or JP-A-59-214852.

The silver halides which form the core of the internally fogged or surface-fogged core/shell silver halide grains may be of the same halogen composition or different halogen compositions. Examples of the internally fogged or surface-fogged silver halide are silver chloride, silver bromochloride, silver bromoidide, and silver bromochloroidide. Although the grain size of these fogged silver halide grains is not particularly limited, an average grain size is preferably 0.01 to  $0.75 \,\mu$ m, and most preferably, 0.05 to  $0.6 \,\mu$ m. The grain shape is also not particularly limited, and may be a regular grain shape. Although the emulsion may be a polydisperse emulsion, it is preferably a monodisperse emulsion (in which at least 95% in weight or number of silver halide grains have a grain size falling within a range of ±40% of the average grain size).

In the present invention, a non-light-sensitive fine grain silver halide is preferably used. The non-lightsensitive fine grain silver halide means silver halide fine grains not sensitive upon imagewise exposure for obtaining a dye image and essentially not developed in development. The non-light-sensitive fine grain silver halide is preferably not fogged beforehand.

50 The fine grain silver halide contains 0 to 100 mol% of silver bromide and may contain silver chloride and/or silver iodide as needed. Preferably, the fine grain silver halide contains 0.5 to 10 mol% of silver iodide.

An average grain size (an average value of equivalent-circle diameters of projected areas) of the fine grain silver halide is preferably 0.01 to 0.5  $\mu$ m, and more preferably, 0.02 to 0.2  $\mu$ m.

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The fine grain silver halide can be prepared by a method similar to a method of preparing normal lightsensitive silver halide. In this preparation, the surface of a silver halide grain need not be subjected to either chemical sensitization or spectral sensitization. However, before the silver halide grains are added to a coating solution, a known stabilizer such as a triazole compound, an azaindene compound, a ben-

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zothiazolium compound, a mercapto compound, or a zinc compound is preferably added. This fine grain silver halide grain-containing layer preferably contains colloidal silver.

A coating silver amount of the light-sensitive material of the present invention is preferably 6.0 g/m<sup>2</sup> or less, and most preferably, 4.5 g/m<sup>2</sup> or less.

5 Known photographic additives usable in the present invention are also described in the above three RDs, and they are summarized in the following Table:

10	RD307105	page 866		pp. 866- 868	page 868	pp. 868- 870	page 873	page 872	(Continued)
15		right	right	648, right m to page right column	right	right	right page column	left- umns	(Con
20	RD18716	page 648, column	page 648, column	page 648, column to 649, right	page 648, column	page 649, column	page 649, r column to p 650, left c	page 650, lef right columns	
25				400	ЦО	ПО	ЦОФ		
30	RD17643	page 23		pp. 23-24	page 24	pp. 24-25	pp. 25-26	page 25, right column	
35			,- agents	sensiti- er- irs		ũ	ıbsorbent, dye, ultra- absorbents	nting	
40	Additives	Chemical sensitizers	Sensitivity- increasing a	Spectral sen zers, super- sensitizers	Brighteners	Antifoggants, stabilizers	Light absorbent, filter dye, ultr violet absorbent	Stain-preventing agents	
45		1.	2.	°.	4.	م	. 9	7.	

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5	RD307105	page 872	pp.874- 875	pp. 873- 874	page 876	PP. 875- 876	pp. 876- 877	pp. 878- 879
10		, left	, left	left	right	right	right	
15	RD18716	page 650, column	page 651, left column	page 651, left column	page 650, right column	page 650, right column	page 650, column	
20	43	25	26	26	27	26-27	27	
25	RD17643	page	page	page 2	page 2	pp. 26	page 2	
30 35	Additives	Dye image- stabilizer	Hardening agents	Binder	Plasticizers, lubricants	Coating aids, surface active agents	Antistatic agents	Matting agent
40	AG	8. st	9. Ha	10. Bj	11. PJ Ju	12. Cc su aç	13. Ar	14. Mã

In order to prevent degradation in photographic properties caused by formaldehyde gas, a compound described in U.S. Patent 4,411,987 or 4,435,503, which can react with formaldehyde and fix the same, is preferably added to the light-sensitive material.

The light-sensitive material of the present invention preferably contains a mercapto compound described in U.S. Patents 4,740,454 and 4,788,132, JP-A-62-18539, and JP-A-1-283551.

The light-sensitive material of the present invention preferably contains compounds which release, regardless of a developed silver amount produced by the development, a fogging agent, a development accelerator, a silver halide solvent, or precursors thereof, described in JP-A-1-106052.

The light-sensitive material of the present invention preferably contains dyes dispersed by methods described in International Disclosure WO 88/04794 and JP-A-1-502912 or dyes described in European Patent 317,308A, U.S. Patent 4,420,555, and JP-A-1-259358.

Various color couplers can be used in the present invention, and specific examples of these couplers are described in patents described in the above-mentioned RD No. 17643, VII-C to VII-G and RD No. 307105, VII-C to VII-G.

Preferable examples of yellow couplers are described in, e.g., U.S. Patents 3,933,501; 4,022,620; 4,326,024; 4,401,752 and 4,248,961, JP-B-58-10739, British Patents 1,425,020 and 1,476,760, U.S. Patents

EP 0 588 331 A1

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3,973,968; 4,314,023 and 4,511,649, and European Patents 249,473A, 447,969A and 482,552A.

Examples of a magenta coupler are preferably 5-pyrazolone type and pyrazoloazole type compounds, and more preferably, compounds described in, for example, U.S. Patents 4,310,619 and 4,351,897, European Patent 73,636, U.S. Patents 3,061,432 and 3,725,067, RD No. 24220 (June 1984), JP-A-60-33552,

- RD No. 24230 (June 1984), JP-A-60-43659, JP-A-61-72238, JP-A-60-35730, JP-A-55-118034, JP-A-60-5 185951, U.S. Patents 4,500,630; 4,540,654 and 4,556,630, and WO No. 88/04795. Examples of a cyan coupler are phenol type and naphthol type ones. Of these, preferable are those described in, for example, U.S. Patents 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; 4,343,011 and 4,327,173, West German Patent Laid-open Application 3,329,729, European Patents 121,365A and 249,453A, U.S. Patents 3,446,622; 4,333,999; 10 4,775,616; 4,451,559; 4,427,767; 4,690,889; 4,254,212 and 4,296,199, and JP-A-61-42658. Also, the pyrazoloazole type couplers disclosed in JP-A-64-553, JP-A-64-554, JP-A-64-555 and JP-A-64-556, and imidazole type couplers disclosed in U.S. Patent 4,818,672 can be used as cyan coupler in the present invention.
- Typical examples of a polymerized dye-forming coupler are described in, e.g., U.S. Patents 3,451,820; 15 4,080,211; 4,367,282; 4,409,320 and 4,576,910, British Patent 2,102,173, and European Patent 341,188A.

Preferable examples of a coupler capable of forming colored dyes having proper diffusibility are those described in U.S. Patent 4,366,237, British Patent 2,125,570, European Patent 96,570, and West German Laid-open Patent Application No. 3,234,533.

Preferable examples of a colored coupler for correcting unnecessary absorption of a colored dye are 20 those described in RD No. 17643, VII-G, RD No. 30715, VII-G, U.S. Patent 4,163,670, JP-B-57-39413, U.S. Patents 4,004,929 and 4,138,258, British Patent 1,146,368 and JP-A-3-223750. A coupler for correcting unnecessary absorption of a colored dye by a fluorescent dye released upon coupling described in U.S. Patent 4,774,181 or a coupler having a dye precursor group which can react with a developing agent to form a dye as a split-off group described in U.S. Patent 4,777,120 may be preferably used. 25

Those compounds which release a photographically useful residue upon coupling may also be preferably used in the present invention. As DIR couplers, i.e., couplers releasing a development inhibitor, those described in the patents cited in the above-described RD No. 17643, VII-F and RD No. 307105, VII-F, JP-A-57-151944, JP-A-57-154234, JP-A-60-184248, JP-A-63-37346, JP-A-63-37350, and U.S. Patents 30

4,248,962 and 4,782,012, may be used together with the above described compound represented by formula (A).

RD Nos. 11449 and 24241, and JP-A-61-201247, for example, disclose couplers which release bleaching accelerator. These couplers effectively serve to shorten the time of any process that involves bleaching. They are effective, particularly when added to light-sensitive material containing tabular silver

- halide grains. Preferable examples of a coupler which imagewise releases a nucleating agent or a development accelerator are preferably those described in British Patents 2,097,140 and 2,131,188, JP-A-59-157638, and JP-A-59-170840. In addition, compounds releasing, e.g., a fogging agent, a development accelerator, or a silver halide solvent upon redox reaction with an oxidized form of a developing agent, described in JP-A-60-107029, JP-A-60-252340, JP-A-1-44940, and JP-A-1-45687, can also be preferably used.
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Examples of other compounds which can be used in the light-sensitive material of the present invention are competing couplers described in, for example, U.S. Patent 4,130,427; poly-equivalent couplers described in, e.g., U.S. Patents 4,283,472, 4,338,393, and 4,310,618; a DIR redox compound releasing coupler, a DIR coupler releasing coupler, a DIR coupler releasing redox compound, or a DIR redox

releasing redox compound described in, for example, JP-A-60-185950 and JP-A-62-24252; couplers 45 releasing a dye which restores color after being released described in European Patent 173,302A and 313,308A; a ligand releasing coupler described in, e.g., U.S. Patent 4,553,477; a coupler releasing a leuco dye described in JP-A-63-75747; and a coupler releasing a fluorescent dye described in U.S. Patent 4,774,181.

The couplers for use in this invention can be introduced into the light-sensitive material by various 50 known dispersion methods.

Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method are described in, e.g., U.S. Patent 2,322,027. Examples of a high-boiling point organic solvent to be used in the oil-in-water dispersion method and having a boiling point of 175°C or more at atmospheric pressure are

phthalic esters (e.g., dibutylphthalate, dicyclohexylphthalate, di-2-ethylhexylphthalate, decylphthalate, bis-55 (2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate, bis(1,1-di-ethylpropyl) phthalate), phosphate or phosphonate esters (e.g., triphenylphosphate, tricresylphosphate, 2-ethylhexyldiphenylphosphate, tricyclohexylphosphate, tri-2-ethylhexylphosphate, tridodecylphosphate, tributoxyethylphosphate, trich-

loropropylphosphate, and di-2-ethylhexylphenylphosphonate), benzoate esters (e.g., 2-ethylhexylbenzoate, dodecylbenzoate, and 2-ethylhexyl-p-hydroxybenzoate), amides (e.g., N,N-diethyldodecaneamide, N,N-diethyllaurylamide, and N-tetradecylpyrrolidone), alcohols or phenols (e.g., isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylate esters (e.g., bis(2-ethylhexyl) sebacate, dioctylazelate, glyceroltributyrate,

- <sup>5</sup> isostearyllactate, and trioctylcitrate), an aniline derivative (e.g., N,N-dibutyl-2-butoxy-5-tert-octylaniline), and hydrocarbons (e.g., paraffin, dodecylbenzene, and diisopropylnaphthalene). An organic solvent having a boiling point of about 30 °C or more, and preferably, 50 °C to about 160 °C can be used as an auxiliary solvent. Typical examples of the auxiliary solvent are ethyl acetate, butyl acetate, ethyl propionate, methylethylketone, cyclohexanone, 2-ethoxyethylacetate, and dimethylformamide.
- Steps and effects of a latex dispersion method and examples of a immersing latex are described in, e.g., U.S. Patent 4,199,363 and German Laid-open Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

Various types of antiseptics and fungicides agent are preferably added to the color light-sensitive material of the present invention. Typical examples of the antiseptics and the fungicides are phenethyl alcohol, and 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol, and 2-(4-thiazolyl)benzimidazole, which are described in JP-A-63-257747, JP-A-62-272248, and JP-A-1-80941.

In the light-sensitive material of the present invention, the sum total of film thicknesses of all hydrophilic colloidal layers at the side having emulsion layers is preferably 28  $\mu$ m or less, more preferably, 23  $\mu$ m or less, much more preferably, 18  $\mu$ m or less, and most preferably, 16  $\mu$ m or less. A film swell speed T<sub>1/2</sub> is

- 20 preferably 30 seconds or less, and more preferably, 20 seconds or less. The film thickness means a film thickness measured under moisture conditioning at a temperature of 25 °C and a relative humidity of 55% (two days). The film swell speed T<sub>1/2</sub> can be measured in accordance with a known method in the art. For example, the film swell speed T<sub>1/2</sub> can be measured by using a swello-meter described by A. Green et al. in Photographic Science & Engineering, Vol. 19, No. 2, pp. 124 to 129. When 90% of a maximum swell film
- thickness reached by performing a treatment by using a color developer at 30 °C for 3 minutes and 15 seconds is defined as a saturated film thickness,  $T_{1/2}$  is defined as a time required for reaching 1/2 of the saturated film thickness.

The film swell speed T<sub>1/2</sub> can be adjusted by adding a film hardening agent to gelatin as a binder or changing aging conditions after coating. A swell ratio is preferably 150% to 400%. The swell ratio is calculated from the maximum swell film thickness measured under the above conditions in accordance with a relation:

(maximum swell film thickness - film thickness)/film thickness.

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In the light-sensitive material of the present invention, a hydrophilic colloid layer (called back layer) having a total dried film thickness of 2 to 20  $\mu$ m is preferably formed on the side opposite to the side having emulsion layers. The back layer preferably contains, e.g., the light absorbent, the filter dye, the ultraviolet absorbent, the antistatic agent, the film hardener, the binder, the plasticizer, the lubricant, the coating aid, and the surfactant, described above. The swell ratio of the back layer is preferably 150% to 500%.

The color photographic light-sensitive material according to the present invention can be developed by conventional methods described in RD. No. 17643, pp. 28 and 29, RD. No. 18716, the left to right columns, page 651, and RD. No. 307105, pp. 880 and 881.

A color developer used in development of the light-sensitive material of the present invention is an aqueous alkaline solution containing as a main component, preferably, an aromatic primary amine color developing agent. As the color developing agent, although an aminophenol compound is effective, a p-phenylenediamine compound is preferably used. Typical examples of the p-phenylenediamine compound are:

- 3-methyl-4-amino-N,N-diethylaniline,
   3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline,
   3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline,
   3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline,
   3-methyl-4-amino-N-ethyl-N-β-methoxyethylaniline,
- described in European Patent 410,450A,

1-(4-amino-3-ethylphenyl)-2,5-bis-(2-hydroxyethyl)pyrrolidine described in JP-A-4-11255, and the sulfates, hydrochlorides and p-toluenesulfonates thereof. The above compounds can be used in a combination of two or more thereof in accordance with the application.

In general, the color developer contains a pH buffering agent such as a carbonate, a borate or a phosphate of an alkali metal, and a development restrainer or an antifoggant such as a chloride, a bromide, an iodide, a benzimidazole, a benzothiazole, or a mercapto compound. If necessary, the color developer may also contain a preservative such as hydroxylamine, diethylhydroxylamine, a sulfite, a hydrazine such

- 5 as N,N-biscarboxymethylhydrazine, a phenylsemicarbazide, triethanolamine, or a catechol sulfonic acid; an organic solvent such as ethyleneglycol or diethyleneglycol; a development accelerator such as benzylal-cohol, polyethyleneglycol, a quaternary ammonium salt or an amine; a dye-forming coupler; a competing coupler; an auxiliary developing agent such as 1-phenyl-3-pyrazolidone; a viscosity-imparting agent; and a chelating agent such as an aminopolycarboxylic acid, an aminopolyphosphonic acid, an alkylphosphonic
- 10 acid, or a phosphonocarboxylic acid. Examples of the chelating agent are ethylene-diaminetetraacetic 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 salts thereof.
- In order to perform reversal development, black-and-white development is performed and then color development is performed. As a black-and-white developer, a well-known black-and-white developing agent, e.g., a dihydroxybenzene such as hydroquinone, a 3-pyrazolidone such as 1-phenyl-3-pyrazolidone, and an aminophenol such as N-methyl-p-aminophenol can be used singly or in a combination of two or more thereof. The pH of the color and black-and-white developers is generally 9 to 12. Although the quantity of
- 20 replenisher of the developers depends on a color photographic light-sensitive material to be processed, it is generally 3 liters or less per m<sup>2</sup> of the light-sensitive material. The quantity of replenisher can be decreased to be 500 m t or less by decreasing a bromide ion concentration in a replenisher. When the quantity of the replenisher is decreased, a contact area of a processing tank with air is preferably decreased to prevent evaporation and oxidation of the solution upon contact with air.
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The contact area of the processing solution with air in a processing tank can be represented by an aperture defined below:

Aperture = [contact area (cm<sup>2</sup>) of processing solution with air]/[volume (cm<sup>3</sup>) of the solution]

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The above aperture is preferably 0.1 or less, and more preferably, 0.001 to 0.05. In order to reduce the aperture, a shielding member such as a floating cover may be provided on the surface of the photographic processing solution in the processing tank. In addition, a method of using a movable cover described in JP-A-1-82033 or a slit developing method descried in JP-A-63-216050 may be used. The aperture is preferably reduced not only in color and black-and-white development steps but also in all subsequent steps, e.g., bleaching, bleach-fixing, fixing, washing, and stabilizing steps. In addition, the quantity of replenisher can be

reduced by using a means of suppressing storage of bromide ions in the developing solution. A color development time is normally 2 to 5 minutes. The processing time, however, can be shortened

by setting a high temperature and a high pH and using the color developing agent at a high concentration.
 The photographic emulsion layer is generally subjected to bleaching after color development. The bleaching may be performed either simultaneously with fixing (bleach-fixing) or independently thereof. In addition, in order to increase a processing speed, bleach-fixing may be performed after bleaching. Also, processing may be performed in a bleach-fixing bath having two continuous tanks, fixing may be performed before bleach-fixing, or bleaching may be performed after bleach-fixing, in accordance with the application.

- 45 Examples of the bleaching agent are compounds of a polyvalent metal, e.g., iron (III); peracids; quinones; and nitro compounds. Typical examples of the bleaching agent are an organic complex salt of iron (III), e.g., a complex salt with an aminopolycarboxylic acid such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, methyliminodiacetic acid, and 1,3-diaminopropanetetraacetic acid, and glycoletherdiaminetetraacetic acid; or a complex salt with citric acid,
- tartaric acid, or malic acid. Of these compounds, an iron (III) complex salt of an aminopolycarboxylic acid such as an iron (III) complex salt of ethylene-diaminetetraacetic acid or 1,3-diaminopropanetetraacetic acid is preferred because it can increase a processing speed and prevent an environmental contamination. The iron (III) complex salt of an aminopolycarboxylic acid is useful in both the bleaching and bleach-fixing solutions. The pH of the bleaching or bleach-fixing solution using the iron (III) complex salt of an aminopolycarboxylic acid is normally 4.0 to 8. In order to increase the processing speed, however,

processing can be performed at a lower pH.

A bleaching accelerator can be used in the bleaching solution, the bleach-fixing solution, and their prebath, if necessary. Examples of a useful bleaching accelerator are: compounds having a mercapto group or a disulfide group described in, for example, U.S. Patent 3,893,858, West German Patents 1,290,812 and 2,059,988, JP-A-53-32736, JP-A-53-57831, JP-A-53-37418, JP-A-53-72623, JP-A-53-95630, JP-A-53-95631, JP-A-53-104232, JP-A-53-124424, JP-A-53-141623, JP-A-53-28426, and RD No. 17129 (July, 1978); thiazolidine derivatives described in JP-A-50-140129; thiourea derivatives described in JP-B-45-8506, JP-A-

- 5 52-20832, JP-A-53-32735, and U.S. Patent 3,706,561; iodide salts described in West German Patent 1,127,715 and JP-A-58-16235; polyoxyethylene compounds descried in West German Patents 966,410 and 2,748,430; polyamine compounds described in JP-B-45-8836; compounds descried in JP-A-49-40943, JP-A-49-59644, JP-A-53-94927, JP-A-54-35727, JP-A-55-26506, and JP-A-58-163940; and a bromide ion. Of these compounds, a compound having a mercapto group or a disulfide group is preferable since the
- 10 compound has a large accelerating effect. In particular, compounds described in U.S. Patent 3,893,858, West German Patent 1,290,812, and JP-A-53-95630 are preferred. A compound described in U.S. Patent 4,552,834 is also preferable. These bleaching accelerators may be added in the light-sensitive material. These bleaching accelerators are useful especially in bleach-fixing of a photographic color light-sensitive material.
- The bleaching solution or the bleach-fixing solution preferably contains, in addition to the above compounds, an organic acid in order to prevent a bleaching stain. The most preferable organic acid is a compound having an acid dissociation constant (pKa) of 2 to 5, e.g., acetic acid, propionic acid, or hydroxy acetic acid.

Examples of the fixing agent used in the fixing solution or the bleach-fixing solution are a thiosulfate
salt, a thiocyanate salt, a thioether-based compound, a thiourea and a large amount of an iodide. Of these compounds, a thiosulfate, especially, ammonium thiosulfate, can be used in the widest range of applications. In addition, a combination of a thiosulfate with a thiocyanate, a thioether-based compound or thiourea is preferably used. As a preservative of the fixing solution or the bleach-fixing solution, a sulfite, a bisulfite, a carbonyl bisulfite adduct, or a sulfinic acid compound described in European Patent 294,769A is preferred.
Further, in order to stabilize the fixing solution or the bleach-fixing solution, various types of aminopolycar-

boxylic acids or organic phosphonic acids are preferably added to the solution.

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

The total time of a desilvering step is preferably as short as possible as long as no desilvering defect occurs. A preferable time is one to three minutes, and more preferably, one to two minutes. A processing temperature is 25 °C to 50 °C, and preferably, 35 °C to 45 °C. Within the preferable temperature range, a desilvering speed is increased, and generation of a stain after the processing can be effectively prevented.

- In the desilvering step, stirring is preferably as strong as possible. Examples of a method of intensifying the stirring are a method of colliding a jet stream of the processing solution against the emulsion surface of the light-sensitive material described in JP-A-62-183460, a method of increasing the stirring effect using rotating means described in JP-A-62-183461, a method of moving the light-sensitive material while the emulsion surface is brought into contact with a wiper blade provided in the solution to cause disturbance on
- 40 the emulsion surface, thereby improving the stirring effect, and a method of increasing the circulating flow amount in the overall processing solution. Such a stirring improving means is effective in any of the bleaching solution, the bleach-fixing solution, and the fixing solution. It is assumed that the improvement in stirring increases the speed of supply of the bleaching agent and the fixing agent into the emulsion film to lead to an increase in desilvering speed. The above stirring improving means is more effective when the bleaching accelerator is used, i.e., significantly increases the accelerating speed or eliminates fixing

interference caused by the bleaching accelerator.

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An automatic developing machine for processing the light-sensitive material of the present invention preferably has a light-sensitive material conveyer means described in JP-A-60-191257, JP-A-60-191258, or JP-A-60-191259. As described in JP-A-60-191257, this conveyer means can significantly reduce carry-over

<sup>50</sup> of a processing solution from a pre-bath to a post-bath, thereby effectively preventing degradation in performance of the processing solution. This effect significantly shortens especially a processing time in each processing step and reduces the quantity of replenisher of a processing solution.

The photographic light-sensitive material of the present invention is normally subjected to washing and/or stabilizing steps after desilvering. An amount of water used in the washing step can be arbitrarily determined over a broad range in accordance with the properties (e.g., a property determined by the substances used, such as a coupler) of the light-sensitive material, the application of the material, the temperature of the water, the number of water tanks (the number of stages), a replenishing scheme representing a counter or forward current, and other conditions. The relationship between the amount of

water and the number of water tanks in a multi-stage counter-current scheme can be obtained by a method described in "Journal of the Society of Motion Picture and Television Engineering", Vol. 64, PP. 248 - 253 (May, 1955). In the multi-stage counter-current scheme disclosed in this reference, the amount of water used for washing can be greatly decreased. Since washing water stays in the tanks for a long period of

- time, however, bacteria multiply and floating substances may be adversely attached to the light-sensitive 5 material. In order to solve this problem in the process of the color photographic light-sensitive material of the present invention, a method of decreasing calcium and magnesium ions can be effectively utilized, as described in JP-A-62-288838. In addition, a germicide such as an isothiazolone compound and a cyabendazole described in JP-A-57-8542, a chlorine-based germicide such as chlorinated sodium isocyanurate,
- and germicides such as benzotriazole, described in Hiroshi Horiguchi et al., "Chemistry of Antibacterial and 10 Antifungal Agents", (1986), Sankyo Shuppan, Eiseigijutsu-Kai ed., "Sterilization, Antibacterial, and Antifungal Techniques for Microorganisms", (1982), Kogyogijutsu-Kai, and Nippon Bokin Bobai Gakkai ed., "Dictionary of Antibacterial and Antifungal Agents", (1986), can be used.

The pH of the water for washing the photographic light-sensitive material of the present invention is 4 to 9, and preferably, 5 to 8. The water temperature and the washing time can vary in accordance with the 15 properties and applications of the light-sensitive material. Normally, the washing time is 20 seconds to 10 minutes at a temperature of 15°C to 45°C, and preferably, 30 seconds to 5 minutes at 25°C to 40°C. The light-sensitive material of the present invention can be processed directly by a stabilizing agent in place of water-washing. All known methods described in JP-A-57-8543, JP-A-58-14834, and JP-A-60-220345 can be

used in such stabilizing processing. 20

> In some cases, stabilizing is performed subsequently to washing. An example is a stabilizing bath containing a dye stabilizing agent and a surface-active agent to be used as a final bath of the photographic color light-sensitive material. Examples of the dye stabilizing agent are an aldehyde such as formalin or glutaraldehyde, an N-methylol compound, hexamethylenetetramine, and an adduct of aldehyde sulfite. Various chelating agents and fungicides can be added to the stabilizing bath.

An overflow solution produced upon washing and/or replenishment of the stabilizing solution can be reused in another step such as a desilvering step.

In the processing using an automatic developing machine or the like, if each processing solution described above is concentrated by evaporation, water is preferably added to correct the concentration.

- The silver halide color light-sensitive material of the present invention may contain a color developing 30 agent in order to simplify processing and increases a processing speed. For this purpose, various types of precursors of a color developing agent can be preferably used. Examples of the precursor are an indoaniline-based compound described in U.S. Patent 3,342,597, Schiff base compounds described in U.S. Patent 3,342,599 and RD Nos. 14850 and 15159, an aldol compound described in RD No. 13924, a metal salt complex described in U.S. Patent 3,719,492, and a urethane-based compound described in JP-A-53-35
- 135628.

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The silver halide color light-sensitive material of the present invention may contain various 1-phenyl-3pyrazolidones in order to accelerate color development, if necessary. Typical examples of the compound are described in JP-A-56-64339, JP-A-57-144547, and JP-A-58-115438.

Each processing solution in the present invention is used at a temperature of 10 °C to 50 °C. Although a 40 normal processing temperature is 33 °C to 38 °C, processing may be accelerated at a higher temperature to shorten a processing time, or image quality or stability of a processing solution may be improved at a lower temperature.

The present invention will be described in greater detail below by way of its examples, but the invention is not limited to these examples. 45

Example 1

(1) Manufacture of supports

50

Supports A to D be	low were manufactured in accordance with the following method.
Support A-1	(polyethylenenaphthalate (PEN):
	thickness 80 μm)
Support A-2	(polyethylenenaphthalate (PEN):
	thickness 122 μm)
Support B-1	(polyethyleneterephthalate (PET):
	thickness 90 μm)
Support C-1	(triacetylcellulose (TAC):

thickness 122 μm)

Supports D-1 to D-3

(mixtures prepared by mixing PEN, PET, PAr, and PCT at the ratios listed in Table 2 below: thickness 80  $\mu$ m)

5 The supports A-1 and A-2: 100 parts by weight of a commercially available polyethylene-2,6naphthalate polymer and 2 parts by weight of Tinuvin P.326 (available from Ciba Geigy Co.) as a ultraviolet absorbent were dried by a conventional method and melted at 300 °C. Thereafter, the resultant material was extruded from a T-die and longitudinally oriented by 3.3 times at 140 °C. Subsequently, the resultant material was laterally oriented by 3.3 times at 130 °C and thermally fixed at 250 °C for six seconds, yielding 10 films 80 μm and 122 μm in thickness.

The support B-1: A commercially available polyethyleneterephthalate polymer was biaxially oriented and thermally fixed in accordance with a conventional method to obtain a 90 µm thick film.

The support C-1: Triacetylcellulose was processed by a regular band-casting process in which methylene chloride/methanol = 82/8 wt ratio, TAC concentration = 13%, and plasticizer (TPP/BDP = 2/1: TPP means triphenylphosphate, BDP means biphenyldiphenylphosphate), thereby manufacturing the support.

The supports D-1 to D-3: In accordance with the formation method of the support A, materials were kneaded and extruded at 280 °C by using a biaxial kneading extruder. The resultant materials were then pelletized and formed into films 80  $\mu$ m in thickness.

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(2) Coating of subbing layers

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A corona discharge treatment was performed on both the surfaces of each of the supports A, B, and D, and a subbing layer with the following composition was formed on each resultant support. The corona discharge treatment was performed for a 30-cm wide support at a rate of 20 m/min by using a Solid-State Corona Processor 6KVA Model available from Pillar Co. It was observed from the read values of a current and a voltage that a treatment of 0.375 kV•A•min/m<sup>2</sup> was performed for each object to be treated. In this treatment, the discharge frequency was 9.6 kHz, and the gap clearance between an electrode and a dielectric roll was 1.6 mm.

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Gelatin	3 g
Distilled water	250 cc
Sodium α-sulfodi-2-ethyl hexylsuccinate	0.05 g
Formaldehyde	0.02 g

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In addition, a subbing layer with the following composition was formed on the support C.

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Gelatin	0.2 g
Salicylic acid	0.1 g
Methanol	15 cc
Acetone	85 cc
Formaldehyde	0.01 g

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(3) Coating of back layer

A back layer was coated on the surface of each of the subbed supports A to D opposite to the surface on which the subbing layer was formed in accordance with the following procedures.

3-1) Preparation of conductive fine grain dispersion (dispersion of tin oxide-antimony oxide composite material)

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230 parts by weight of stannic chloride hydrate and 23 parts by weight of antimony trichloride were dissolved in 3,000 parts by weight of ethanol to prepare a homogeneous solution. An aqueous 1 N sodium hydroxide solution was dropped into the resultant solution until the pH became 3, yielding a colloidal coprecipitate of stannic oxide and antimony oxide. The obtained coprecipitate was left to stand at 50 °C for

24 hours to yield a reddish blown colloidal precipitate.

The resultant reddish blown colloidal precipitate was separated by centrifugal separation. To remove excess ions, the precipitate was washed three times with water through centrifugal separation.

200 parts by weight of the colloidal precipitate from which excess ions were removed were redispersed in 1,500 parts by weight of water, and the resultant dispersion was sprayed into a calcinating furnace heat up to 600 ° C, forming a bluish fine grain powder of a tin oxide-antimony oxide composite material with an average grain size of 0.2 μm. The specific resistance of this fine grain powder was 25 Ω • cm.

A mixture of 40 parts by weight of the above fine grain powder and 60 parts by weight of water was controlled to have a pH of 7.0 and coarsely dispersed by a stirring machine. Thereafter, the resultant *10* dispersion was further dispersed for a residence time of 30 minutes by using a horizontal sand mill (DYNOMILL (tradename); available from WILLY A. BACHOFENAG).

3-2) Preparation of back layer

The following formulation A was so coated as to have a dry film thickness of 0.3 μm and dried at 130 °C for 30 seconds. The following coating solution (B) for forming a coating film was further coated on the resultant film so as to have a dry film thickness of 0.1 μm and dried at 130 °C for two minutes.

20	[Formulation A]					
	Above-mentioned conductive fine grain dispersion Gelatin Water	10 parts by weight 1 part by weight 27 parts by weight				
25	Methanol Resorcin Polyoxyethylenenonyl phenylether	60 parts by weight 2 parts by weight 0.01 part by weight				

[Coating solution (B) for forming coating film]						
Cellulose triacetate	1 part by weight					
Acetone	70 parts by weight					
Methanol	15 parts by weight					
Dichloromethylene	10 parts by weight					
p-chlorophenol	4 parts by weight					

## (4) Heat treatment for supports

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After the subbing layer and the back layer were coated in accordance with the above processes, a heat treatment was performed under the conditions shown in Table 2. The heat treatment was performed by winding each resultant support around a core 30 cm in diameter with the subbed surface located outside.

## 45 (5) Measurement of bending modulus

A bending modulus which is the most important factor among other dynamic strengths of a support in decreasing the thickness of the support was measured. The measurement of the bending modulus was performed by a method called a loop stiffness method. That is, a 35-mm wide sample which was slit, i.e.,

<sup>50</sup> cut in the longitudinal direction was formed into a torus with a circumference of 10 cm and placed horizontally. A load applied when the torus deformed by 12 mm in the direction of the diameter was measured as the bending modulus. The measurement was performed at a temperature of 25 °C and a relative humidity of 60% such that the subbing layer of each sample was located inside the torus.

The measurement results are summarized in Table 2. As is apparent from Table 2, PEN with a thickness of 80  $\mu$ m and PET with a thickness of 90  $\mu$ m exhibited the values of bending modulus nearly equivalent to that of TAC with a thickness of 122  $\mu$ m. When the thickness of PEN was increased up to 122  $\mu$ m, the same thickness as that of TAC, the bending modulus of PEN was three times that of TAC.

	6				T			
5 10	Bending modulus (Loop sfiffness) [(	34	116	35	36	30	28	27
20	Heat treatment	110°C, 24 hrs	Ŧ	60°C, 24 hrs	None	85°C, 24 hrs	71°C, 24 hrs	108°C, 24 hrs
25 <b>Z</b>	Thickness H	80	122	06	122	80	Ξ	T
30	Tg [g]	119	E	69	120	95	81	118
35	ion, wt%)					(60/40)	(40/60)	(50/50)
40	Support (Composition,	PEN (100)	=	PET ( "	TAC ("	PET	PEN/PET	PAr/PCT (50/50)
	No.	A-1	A-2	B-1	C-1	D-1	D-2	D- 3

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(6) Coating of light-sensitive layers

Layers with the following compositions were multicoated on each of the supports formed by the above method, manufacturing multilayered color light-sensitive materials. Note that the symbols representing the individual supports are used directly to represent the corresponding multilayered color light-sensitive materials. As an example, a light-sensitive material obtained by coating these light-sensitive layers on the support A-1 is labeled a multilayered color light-sensitive material A-1.

Compositions of Light-sensitive Layers

The main materials used in the individual layers are classified as follows.

-	

ExC	Cyan coupler	UV	Ultraviolet absorbent
ExM	Magenta coupler	HBS	High-boiling organic solvent
ExY	Yellow coupler	н	Gelatin hardener
ExS	Sensitizing dye		

The number corresponding to each component indicates the coating amount in units of  $g/m^2$ . The coating amount of a silver halide is represented by the amount of silver. The coating amount of each sensitizing dye is represented in units of mols per mol of a silver halide in the same layer.

1st layer (Antihalation layer)							
Black colloidal silver	silver	0.18					
Gelatin 1.40							
ExM-1		0.18					
ExF-1		$2.0 \times 10^{-3}$					
HBS-1		0.20					

25	2nd layer (Interlayer)					
	Emulsion G silver	0.065				
	2,5-di-t-pentadecylhydroquinone	0.18				
	ExC-2	0.020				
	UV-1	0.060				
30	UV-2	0.080				
	UV-3	0.10				
	HBS-1	0.10				
	HBS-2	0.020				
35	Gelatin	1.04				

3rd layer (Low-speed red-sensitive emulsion layer)		
Emulsion A	silver	0.25
Emulsion B	silver	0.25
ExS-1		6.9 × 10 <sup>−5</sup>
ExS-2		1.8 × 10 <sup>−5</sup>
ExS-3		3.1 × 10 <sup>−4</sup>
ExC-1		0.17
ExC-3		0.030
ExC-4		0.10
ExC-5		0.020
ExC-7		0.0050
A-(44)		0.010
Cpd-2		0.025
HBS-1		0.050
HBS-5		0.050
Gelatin		0.87

4th layer (Medium-speed red-sensitive emulsion layer)		
Emulsion D	silver	0.70
ExS-1		$3.5 \times 10^{-4}$
ExS-2		1.6 × 10 <sup>-5</sup>
ExS-3		5.1 × 10 <sup>-4</sup>
ExC-1		0.13
ExC-2		0.060
ExC-3		0.0070
ExC-8		0.094
ExC-5		0.025
ExC-7		0.0010
A-(44)		0.0070
Cpd-2		0.023
HBS-1		0.060
HBS-4		0.050
Gelatin		0.75

5th layer (High-speed red-sensitive emulsion layer)		
Emulsion E	silver	1.40
ExS-1		2.4 × 10 <sup>-4</sup>
ExS-2		$1.0 \times 10^{-4}$
ExS-3		3.4 × 10 <sup>-4</sup>
ExC-1		0.12
ExC-3		0.045
ExC-6		0.020
A-(44)		0.025
Cpd-2		0.050
HBS-1		0.22
HBS-2		0.10
Gelatin		1.20

6th layer (Interlayer)		
Cpd-1 0.10		
Cpd-4 0.050		
HBS-1 0.50		
Gelatin 1.10		

7th layer (Low-speed green-sensitive emulsion layer)		
Emulsion C	silver	0.35
ExS-4		3.0 × 10 <sup>-5</sup>
ExS-5		2.1 × 10 <sup>-4</sup>
ExS-6		$8.0 \times 10^{-4}$
ExM-1		0.010
ExM-2		0.33
ExM-3		0.086
ExY-1		$8.0 \times 10^{-3}$
A-(30)		5.0 × 10 <sup>-3</sup>
HBS-1		0.20
HBS-3		0.010
HBS-5		0.15
Gelatin		0.73

8th layer (Medium-speed green-sensitive emulsion layer)		
Emulsion D	silver	0.80
ExS-4		3.2 × 10 <sup>−5</sup>
ExS-5		$2.2 \times 10^{-4}$
ExS-6		8.4 × 10 <sup>-4</sup>
ExM-2		0.13
ExM-3		0.030
A-(27)		7.0 × 10 <sup>−3</sup>
A-(23)		$4.0 \times 10^{-3}$
HBS-1		0.16
HBS-3		8.0 × 10 <sup>-3</sup>
HBS-4		0.040
Gelatin		0.90

9th layer (High-spe	9th layer (High-speed green-sensitive emulsion layer)		
Emulsion E ExS-4 ExS-5 ExS-6 ExC-1 ExM-1	•	$\begin{array}{c} 1.25\\ 3.7\times10^{-5}\\ 8.1\times10^{-5}\\ 3.2\times10^{-4}\\ 0.010\\ 0.030\end{array}$	
ExM-4 ExM-5 A-(12) Cpd-3 HBS-1 HBS-2 HBS-3 Gelatin		$\begin{array}{c} 0.10\\ 0.024\\ 1.0 \times 10^{-3}\\ 0.040\\ 0.25\\ 0.10\\ 8.0 \times 10^{-3}\\ 1.44\end{array}$	

10th layer (Yellow filter layer)		
Yellow colloidal silver Cpd-1 HBS-1 Gelatin	silver	0.030 0.16 0.60 0.60

11th layer (Low-speed blue-sensitive emulsion layer)		
Emulsion C	silver	0.18
ExS-7		8.6 × 10 <sup>-4</sup>
ExY-1		0.020
ExY-2		0.22
ExY-3		0.50
ExY-4		0.020
HBS-1		0.15
HBS-4		0.15
Gelatin		1.10

12th layer (Medium-speed blue-sensitive emulsion layer)		
Emulsion D silver	0.40	
ExS-7 ExC-7	$7.4 \times 10^{-4}$ 5.0 × 10^{-3}	
ExY-2	0.050	
ExY-3	0.10	
A-(35)	$2.0 \times 10^{-3}$	
HBS-1	0.050	
Gelatin	0.78	

13th layer (high-speed blue-sensitive emulsion layer)		
Emulsion F ExS-7 ExY-2 ExY-3 A-(42) HBS-1 HBS-5	silver	$\begin{array}{c} 1.00\\ 4.0 \times 10^{-4}\\ 0.10\\ 0.10\\ 1.5 \times 10^{-3}\\ 0.040\\ 0.030\end{array}$
Gelatin		0.86

14th layer (1st protective layer)		
Emulsion G	0.20	
UV-4		0.11
UV-5		0.17
HBS-1		5.0 × 10 <sup>-2</sup>
Gelatin		1.00

15th layer (2nd protectiv	e layer)			
H-1	0.40			
B-1 (diameter 1.7 μm) 5.0 × 10 <sup>-2</sup>				
B-2 (diameter 1.7 μm) 0.10				
B-3 0.10				
S-1 0.20				
Gelatin	1.20			

<sup>10</sup> In addition to the above components, to improve shelf stability, processability, a resistance to pressure, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained W-1 to W-3, B-4 to B-6, F-1 to F-17, iron salt, lead salt, gold salt, platinum salt, iridium salt, palladium salt, and rhodium salt.

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In	Table 3	,	

(1) The emulsions A to F were subjected to reduction sensitization during grain preparation by using thiourea dioxide and thiosulfonic acid in accordance with the examples in JP-A-2-191938.

(2) The emulsions A to F were subjected to gold sensitization, sulfur sensitization, and selenium sensitization in the presence of the spectral sensitizing dyes described in the individual light-sensitive layers and sodium thiocyanate in accordance with the examples in JP-A-3-237450.

				Table 3		
	Average AgI content	Average grain size	Variation coefficient (%) related to grain size	Diameter/ thickness ratio	Silver amount ratio [core/intermediate/ shell] (Ag1 content)	Grain structure/ shape
Emulsion		0.45	27	1	[1/3] (13/1)	Double structure octahedral grain
Emulsion B		0.70	14	1	[3/7] (25/2)	Double structure octahedral grain
Emulsion		0.55	25	7		Uniform structure tabular grain
Emulsion		0.65	25	9	[12/59/29] (0/11/8)	Triple structure tabular grain
Emulsion			23	ß	[ 8/59/33] (0/11/8)	Triple structure tabular grain
Emulsion			25	e	[37/63] (34/3)	Double structure tabular grain
Emulsion G		0.07	15	1		Uniform structure fine grain

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(3) The preparation of tabular grains was performed in accordance with the examples in JP-A-1-158426, in which low-molecular weight gelatin was used.

(4) Dislocation lines as described in JP-A-3-237450 were observed in tabular grains and regular crystal grains having a grain structure when a high-voltage electron microscope was used.

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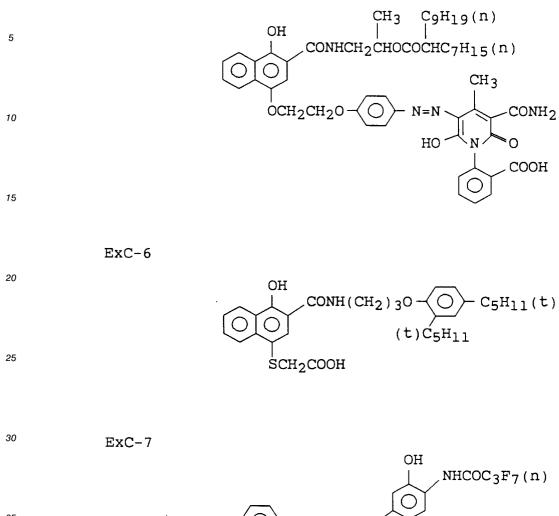
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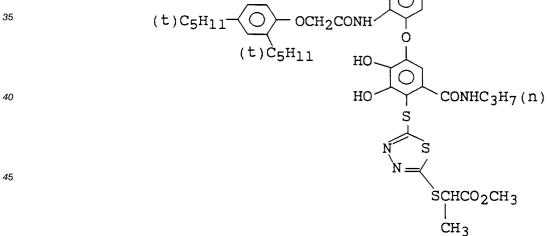
ExC-1 OH  $CONH(CH_2)_3OC_{12}H_{25}(n)$ 10  $(1)C_4H_9OCNH$ 15 Ô ExC-2 20 OH  $CONHC_{12}H_{25}(n)$ Ο О 25 OH NHCOCH3 N = NOCH2CH2O  $\bigcirc$ 30 NaOSO2 SO<sub>3</sub>Na 35 ExC-3 OH  $CONH(CH_2)_3OC_{12}H_{25}(n)$  $\bigcirc$ 40 (i)C4H9OCONH OCH2CH2SCH2CO2H 45 ExC-4 OH  $30 - C_{5H_{11}}(t)$ (t)C<sub>5H11</sub> 50  $CONH(CH_2)_{3}O \bigcirc$ 

(i)C4H9OCNH

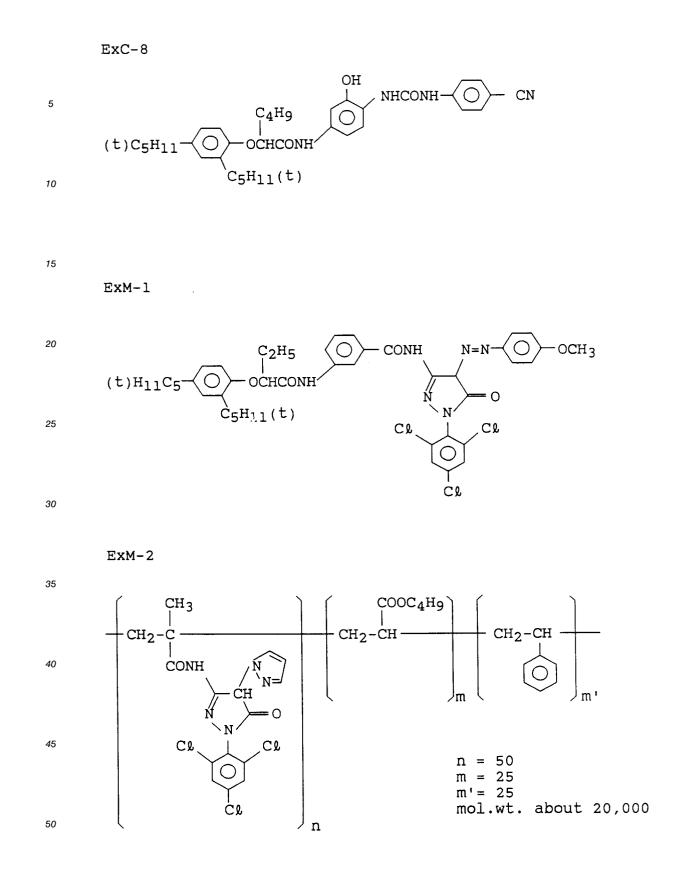
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ExC-5

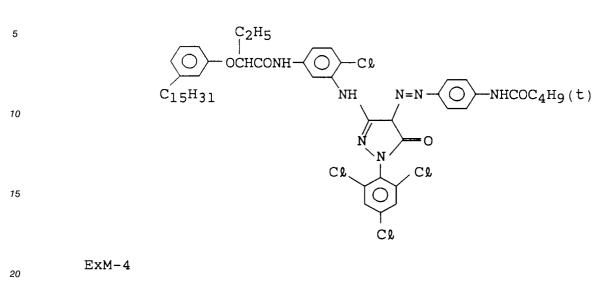


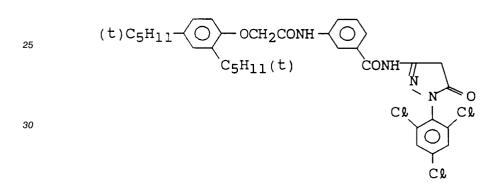


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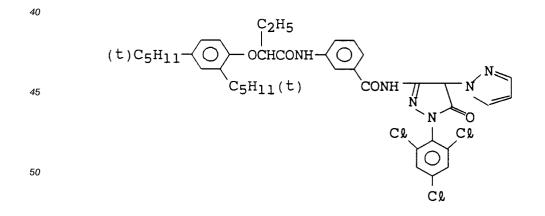
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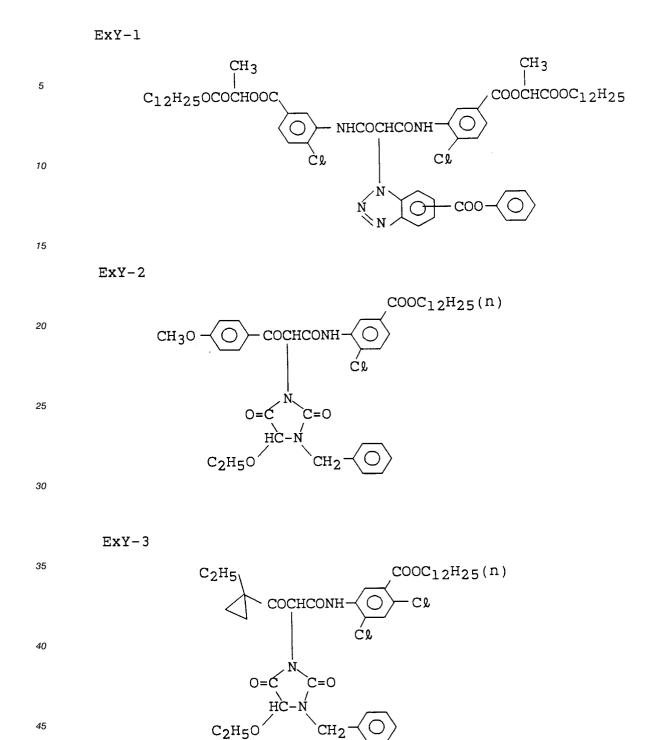




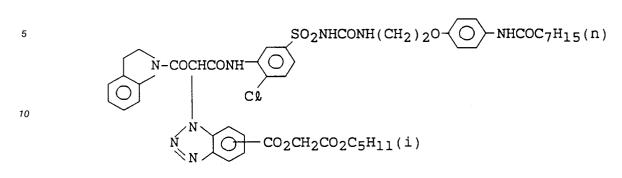
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ExM-5

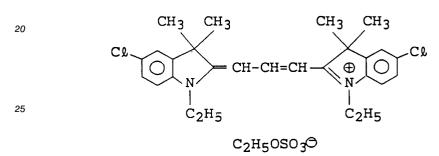






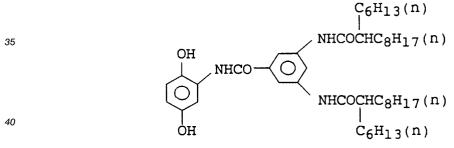


ExF-1

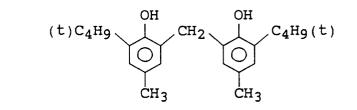


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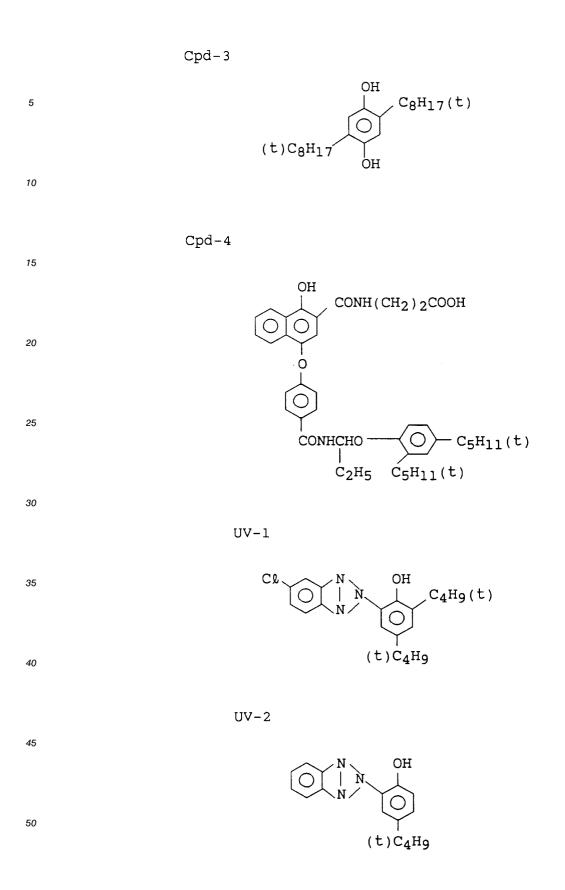
Cpd-1



45 Cpd-2

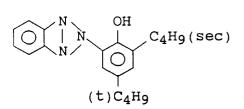


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UV-3



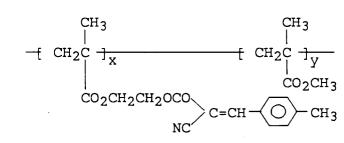


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UV-4



x:y = 70:30 (wt%)

UV-5

 $(C_2H_5)_2NCH=CH-CH=C$ 30

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HBS-1 Tricresylphosphate

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HBS-2 Di-n-butylphtalate

<sup>45</sup> HBS-3

$$(t)C_{5H_{11}} \xrightarrow{O_{2H_{5}}} OCHCONH \xrightarrow{O_{$$

HBS-4 Di (2-ethylhexyl) phthalate

HBS-5 Triisononylphosphate

ExS-1  
ExS-1  

$$C_2H_5$$
  
 $C_2H_5$   
 $C_2H_5$   

20

35

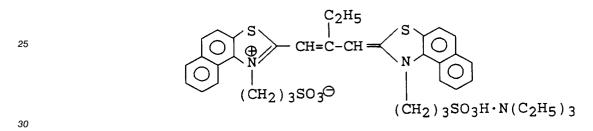
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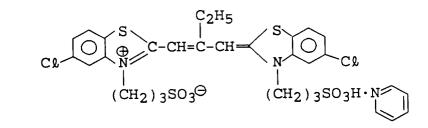
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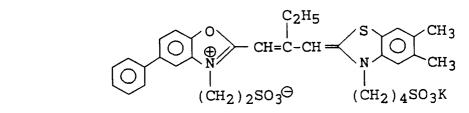
ExS-2



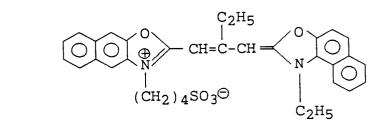
ExS-3

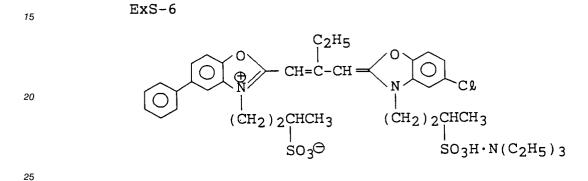


ExS-4

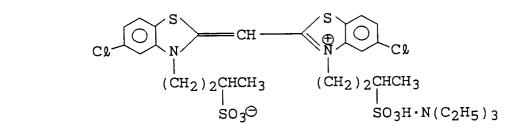


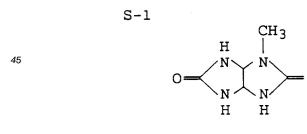






ExS-7





H-1  $CH_2=CH-SO_2-CH_2-CONH-CH_2$  $CH_2 = CH - SO_2 - CH_2 - CONH - CH_2$ 

B-1 10

5

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$$- \begin{array}{c} CH_{3} & CH_{3} \\ - CH_{2} - C \end{array} \\ - CH_{2} - C \end{array} \\ COOH \\ COOH \\ COOCH_{3} \end{array}$$

<sup>20</sup> B-2  

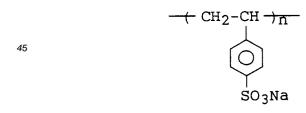
$$\xrightarrow{CH_3} \xrightarrow{CH_3} x/y = 40/60$$
<sup>25</sup> COOH COOCH<sub>3</sub>

30

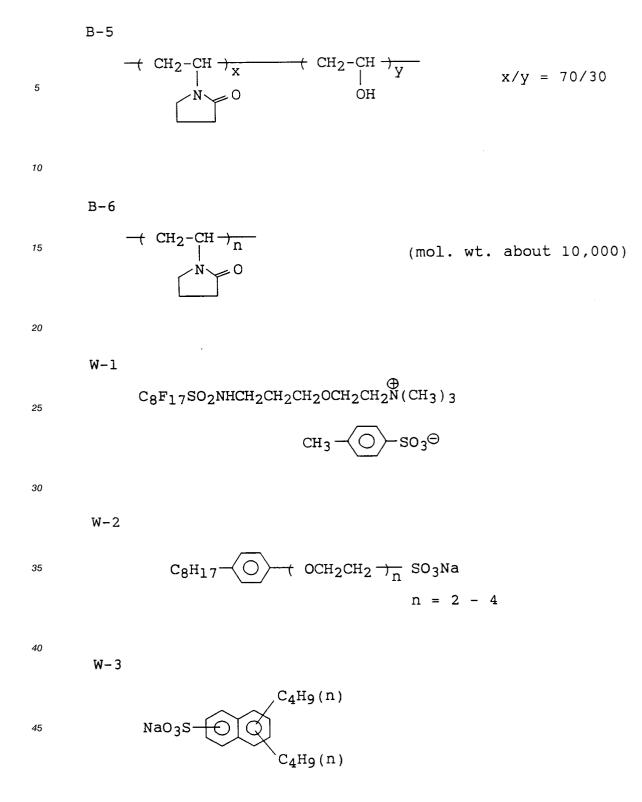
 $(CH_3)_{3}SiO \leftarrow CH_3 \qquad CH_3 \qquad H_3 \qquad H_3$ 35

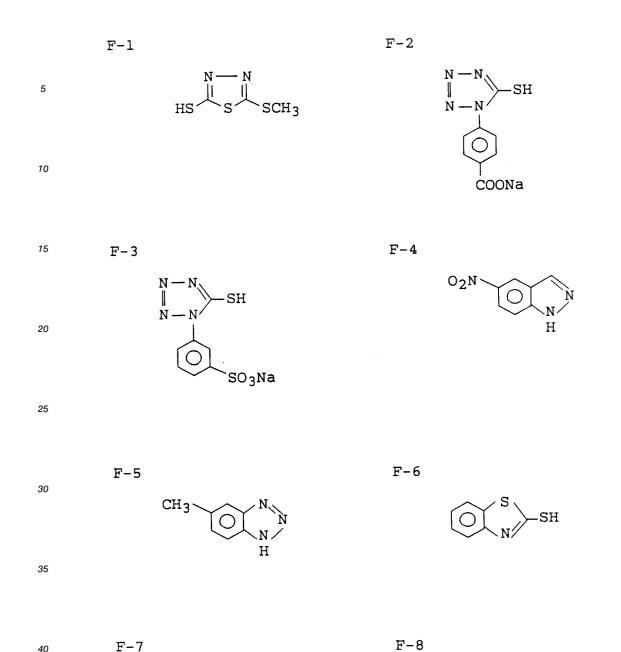
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B-4

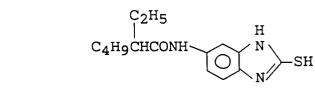


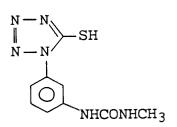
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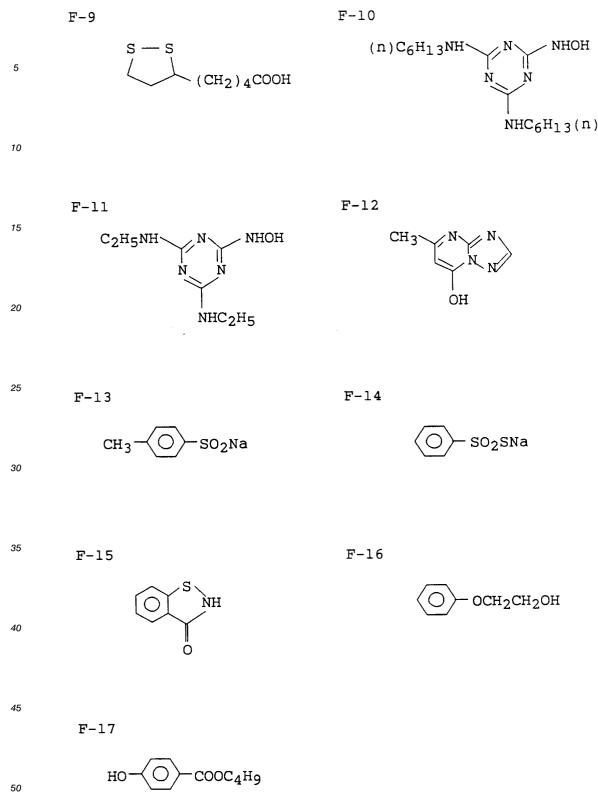




40 F-7

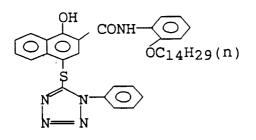






Subsequently, multilayered color light-sensitive materials were formed following the same procedures as for the multilayered color light-sensitive materials A-1 and C-1 except that A-(30) used in the 7th greensensitive emulsion layer, A-(27) and A-(23) used in the 8th green-sensitive emulsion layer, and A-(12) in the 55 ninth green-sensitive emulsion layer were replaced with equal molar quantities of a comparative compound (1) represented by the following formula. These multilayered color light-sensitive materials were labeled A-3 and C-2, respectively.

#### Comparative compound (1)



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Each multilayered color light-sensitive material thus manufactured was slit into a film 35 mm wide and 1.15 m long, and perforations with dimensions of 2 mm × 2.8 mm were formed with an interval of 4.75 mm at positions 2 mm from the both ends in the widthwise direction of the film as same as those in a current 135 format. Each resultant film was wound around a spool 14 mm in diameter and set in a 135-size magazine, forming a photographing film similar to the current 135-format film. These films were labeled Group I.

Separately, perforations with the same dimensions as described above were formed with an interval of 31.7 mm at positions 2 mm from the both ends in the widthwise direction of a film. Each resultant film was wound around a spool 8 mm in diameter to form a photographing film. These films were labeled Group II.

A mannequin (upper half) placed with a resolving power chart and a Macbeth color checker chart was photographed under the following conditions, in which Fuji Zoom Cardia 800 (available from Fuji Photo Film

- <sup>25</sup> Co. Ltd.), for the Group I films, or Fuji Zoom Cardia 800 remodelled such that the area of an imaging area was 5.01 cm<sup>2</sup> (30.0 mm  $\times$  16.7 mm, aspect ratio 1.80) and a film with two perforations per frame could be fed, for the Group II films, was used. Photographing was similarly performed by using the Group II films by changing only the area of an imaging area to 2.55 cm<sup>2</sup> (21.4 mm  $\times$  11.9 mm, aspect ratio 1.8). The resultant films were labeled Group III.
- In this photographing, the distance was set such that a complete view of a main portion of the object to be photographed could be photographed in an imaging area (an exposure portion in a frame) when the Group I films were used. When the films of Groups II and III were to be used, the photographing was performed such that the same complete view was photographed in an image portion by performing a zooming operation without changing the set distance.
- To evaluate a color reproducibility, the color checker chart was separately photographed at a closer distance.

)	Condition	Light source	Contrast of object	Background	Remarks
	А	Daylight (clear)	High	Distant views of trees and mountains	Both sunshine and shadow
	В	Daylight (cloudy)	Low	ditto	
	С	Strobe Light	High	Light gray wall	

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The photographed films were processed in accordance with the following color developing steps by using processing solutions with the following compositions. Note that the processing was performed by using the processing solutions obtained after continuous (running) processing was performed for a sample, which was separately imagewise-exposed, at a rate of 1 m<sup>2</sup>/day for 15 days.

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The processing steps and the compositions of the processing solutions were as follows.

Step	Time	Temperature	Quantity of replenisher*	Tank volume
Color development	3 min. 05 sec.	38.0 ° C	23 m l	10 l
Bleaching	50 sec.	38.0 ° C	5 m t	5 l
Bleach-fixing	50 sec.	38.0 ° C	-	5 l
Fixing	50 sec.	38.0 ° C	16 m l	5 l
Washing	30 sec.	38.0 ° C	34 m t	3.5 l
Stabilization (1)	20 sec.	38.0 ° C	-	3 l
Stabilization (2)	20 sec.	38.0 ° C	20 m l	3 l
Drying	1 min. 30 sec.	60 ° C		

\* The quantity of replenisher was a quantity per 1.1 m of a 35-mm wide sample (corresponding to one 24-Ex. film)

The stabilizing solution was used by a counter flow system from (2) to (1), and the overflow solution of the washing solution was introduced entirely to the fixing bath. The replenishment of the bleach-fixing solution was performed by forming notches in the upper portions of the bleaching tank and the fixing tank of the automatic developing machine so that the overflow solution produced when the replenishers were supplied to the bleaching and fixing tanks was flowed entirely to the bleach-fixing bath. Note that the quantities of the developing solution, the bleaching solution, the bleach-fixing solution, and the fixing solution carried over to the bleaching step, the bleach-fixing step, the fixing step, and the washing step were 2.5 m $\ell$ , 2.0 m $\ell$ , 2.0 m $\ell$ , and 2.0 m $\ell$ , respectively, per 1.1 m of the 35-mm wide light-sensitive material. The crossover time of each step was six seconds, and this time was included in the processing time of each previous step.

The compositions of the processing solutions are presented below.

Color developing solution

#### 

	Tank solution (g)	Replenisher (g)
Diethylenetriamine pentaacetic acid	2.0	2.0
1-hydroxyethylidene-1,1-diphosphonic acid	2.0	2.0
Sodium sulfite	3.9	5.1
Potassium carbonate	37.5	39.0
Potassium bromide	1.4	0.4
Potassium iodide	1.3 mg	-
Hydroxylamine sulfate	2.4	3.3
2-methyl-4-[N-ethyl-N-( <i>β</i> -hydroxyethyl) amino]aniline sulfate	4.5	6.0
Water to make	1.0 l	1.0 l
pH (controlled by potassium hydroxide and sulfuric acid)	10.05	10.15

Bleaching solution

50		Tank solution (g)	Replenisher (g)
	Ammonium 1,3-diaminopropane tetraacetato-ferrate(III) monohydrate	130	195
	Ammonium bromide	70	105
	Ammonium nitrate	14	21
	Hydroxyacetic acid	50	75
55	Acetic acid	40	60
	Water to make	1.0 l	1.0 l
	pH (controlled by ammonia water)	4.4	4.4

#### Bleach-fixing tank solution

A solution mixture (volume ratio = 15 : 85) of the above bleaching tank solution and the following fixing tank solution.

(pH 7.0) 5

Fixing solution

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)		Tank solution (g)	Replenisher (g)
	Ammonium sulfite	19	57
	Aqueous ammonium thiosulfate solution (700 g/ $l$ )	280 l	840 l
	Imidazole	15	45
5	Ethylenediamine tetraacetic acid	15	45
	Water to make	1.0 l	1.0 l
	pH (controlled by ammonia water and acetic acid)	7.4	7.45

#### 20 Washing solution

Tap water was supplied to a mixed-bed column filled with an H type strongly acidic cation exchange resin (Amberlite IR-120B: available from Rohm & Haas Co.) and an OH type strongly basic anion exchange resin (Amberlite IR-400) to set the concentrations of calcium and magnesium to be 3 mg/t or less. 25 Subsequently, 20 mg/l of sodium dichloroisocyanurate and 150 mg/l of sodium sulfate were added. The pH of the solution ranged from 6.5 to 7.5.

Stabilizing solution

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		common to tank solution and replenisher (g)
35	Sodium p-toluenesulfinate	0.03
	Polyoxyethylene-p-monononylphenylether (average degree of polymerization 10)	0.2
	Disodium ethylenediaminetetraacetate	0.05
	1,2,4-triazole	1.3
40	1,4-bis(1,2,4-triazole-1-ylmethyl) piperazine	0.75
	Water to make	1.0 L
	рН	8.5

These color negative films obtained through the above processing were printed onto Fuji Color Paper, Super FA, Type II (commercially available from Fuji Photo Film Co., Ltd.) at magnifications of 5 times, 7 45 times, and 9.5 times for the Group I films, the Group II films, and the Group III films, respectively, by using Fuji Enlarger A690 Professional (commercially available from Fuji Photo Film Co., Ltd.). CP-43FA was used in this color development.

The resultant prints were so cut as to leave only image portions behind, and the sharpness of each print was evaluated on a gray plate (reflection density 0.18) under a fluorescent lamp for color evaluation by ten 50 male monitors and ten female monitors.

The evaluation was performed by using the print obtained from the film made from the multilayered color light-sensitive material C-1 of Group I as a reference and sequentially comparing this reference with other prints one at a time. A print found to be better than the reference was given +1, a print found to be

equivalent to the reference or difficult to determine was given 0, and a print found to be worse than the 55 reference was given -1. After the determination, an arithmetic means of these values was calculated for each print.

The color reproducibility was evaluated by measuring the cyan density of a magenta dye image of the color checker chart photographed in a color negative film and checking the degree of color turbidity by obtaining the difference with respect to the value of the multilayered color light-sensitive material C-1 as a reference.

5 A part of the results is shown in Table 4 below.

10 15		Comparative example	= =	Present invention " Comparative example Present invention	Comparative example Present invention " (Continued)
	(				
20	Color reprodu- cibility	0.00 0.00 (Reference)	0.00	-0.02 -0.01 +0.11 -0.02	0.00 -0.02 -0.02 -0.02
25		ice )			
30 <del>4</del> U	Sharpness	+0.75 0.00 (Reference)	+0.70	+0.90 +0.90 -0.10 +0.50	-0.50 +0.80 +0.60 +0.85
35 35	spool diame- ter [mm]	14		8	
40	Support Mixing ratio (wt%) is given in parentheses	PEN (100) TAC (100)	PEN/PET (60/40) PAr/PCT (50/50)		TAC ( " ) PEN/PET (60/40) " (40/60) PAr/PCT (50/50)
45	No.	A-1 C-1	D-1 D-3	A-1 A-2 A-3 B-1	C-1 D-1 D-2 D-3
50 55	Film group Area of imaging area is given in parentheses	I Current 135 format	(8.64 cm <sup>2</sup> )	II Two perforations per frame (5.01 cm <sup>2</sup> )	

## EP 0 588 331 A1

5 10	Remarks	Comparative example	=	Ξ	Ξ	=
15	Color reprodu- cibility	-0.02	-0.02	0.00	-0.02	-0.02
20 25 <b>寸</b>	Sharpness	-0.30	-0.80	-1.00	-0.60	-0.55
25 <b>4</b> Japle T	Spool diame- ter ss [mm]			8	0	(0)
35	Support Mixing ratio (wt%) is given in parentheses	PEN (100)	PET ( " )	TAC ( " )	PEN/PET (60/40)	PAr/PCT (50/50)
40	No.	A-1	B-1	C-1	D-1	D-3
<i>4</i> 5 50	Film group Area of imaging area is given in parentheses	III	Two perforations	per frame	(2.55 cm <sup>2</sup> )	

Table 4 reveals that the films of Group II each having the polyester support were found to be better in sharpness than those of Group I which were current 135-format films. The reason for this is considered that 55 the flatness of an imaging area to be exposed could not be maintained during photographing because the number of perforations per frame was large in the films of Group I. In fact, some monitors backed up this by pointing out that blurs were found in peripheral portions or central portions of these prints. On the other

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hand, the films of Group III each having an imaging area of 3 cm<sup>2</sup> or less was found to be obviously poor in sharpness, demonstrating that it is difficult to reduce the size of an imaging area to 3 cm<sup>2</sup> or less while maintaining the image quality. In addition, as can be readily seen by comparing the multilayered color lightsensitive material A-1 of the present invention, the comparative light-sensitive material C-1, and the

multilayered color light-sensitive materials A-3 and C-2 formed by replacing a compound represented by 5 Formula (A) with the comparative compound (1), A-1 and C-1 were superior to A-3 and C-2 and A-1 was superior to C-1 in sharpness.

The multilayered color light-sensitive materials A-1 of the present invention and comparative lightsensitive material C-1 using a compound represented by Formula (A) obviously caused less color turbidity

- than and were therefore superior in color reproducibility to A-3 and C-2 having the comparative compound 10 (1) in place of the compound represented by Formula (A). In addition, the films of Groups II and III having reduced imaging areas were improved in color reproducibility compared to the films of Group I having large imaging areas although the differences were small. The reason for this is unknown, but it is estimated that this was caused by some dynamic factor applied on a hydrophilic colloid layer when a film was wound around a spool.
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Note that when the multilayered color light-sensitive material A-1, which was slit into a 35-mm wide film and cut by a length of 1.65 m corresponding to that of a current 135-format film of 36 exposures, was wound around a spool 14 mm in diameter, it was difficult to fit the spool in a 135-format magazine. In contrast, a film wound around a spool 8 mm in diameter was easy to fit in a magazine, and there was an extra space capable of containing a longer film. This means that the number of exposures can be increased

in the current magazine or the magazine can be made thin without decreasing the number of exposures. This, taken into consideration with the fact that the image quality is not impaired at all even by reducing the area of an imaging area to be exposed to be smaller than that of the current format, implies that

miniaturization of cameras is possible.

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## Example 2

PBC-2, PBC-3, PBC-6, PBC-9, PBC-10, and PBB-3 exemplified as polyester compounds were used to perform melting, biaxial orientation, and thermal fixing in accordance with the method described in Example 1, forming supports 80 µm thick. A subbing layer and a back layer were coated on each support, and a 30 heat treatment was performed for each resultant support at a temperature lower by 10°C than the glass transition point (Tg) of each polyester compound. Layers with the compositions shown in Example 1 were multi-coated on each of these supports to manufacture multilayered color light-sensitive materials.

The samples thus manufactured were cut and processed following the same procedures as for the photographing films of Group II described in Example 1, and the sharpness and the color reproducibility of 35 each resultant sample were evaluated by comparing with those of the film C-1 of Group I in Example 1 as a reference.

As a result, substantially the same evaluations as those of A-1 of Group II in Example 1 could be obtained from the multilayered color light-sensitive materials manufactured by using these six types of polyester supports. 40

## Example 3

The multilayered color light-sensitive materials A-1, D-1, and D-3 manufactured in Example 1 were processed to have a width of 24 mm, and perforations were formed in the both side edges in the 45 longitudinal direction of each resultant film such that one perforation was formed per frame in each side edge. Each resultant film was put into the film cartridge described in JP-A-2-273740. A camera was also remodeled so as to be able to load this cartridge. An object to be photographed was photographed following the same procedures as in Example 1 such that the size of an imaging area was 30.0 mm × 12.0 mm (area of imaging area to be exposed 3.60 cm<sup>2</sup>, aspect ratio 2.5).

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In addition, the same samples were processed to have a width of 24 mm, and perforations were formed in one side edge in the longitudinal direction of each resultant sample such that one perforation was formed per frame. Each resultant film was put into the cartridge described in JP-A-2-273740. Photographing was similarly performed such that the imaging area size was 30.0 mm × 21.4 mm (area of imaging area to be

exposed 6.42 cm<sup>2</sup>, aspect ratio 1.4) and was 30.0 mm × 16.7 mm (area of imaging area to be exposed 5.01 55 cm<sup>2</sup>, aspect ratio 1.80). In this photographing, a feed length of one frame of the film was set to 31.7 mm in correspondence with the imaging area size described above.

The distance was determined such that an object to be photographed (the upper half of a mannequin with a resolving power chart and a color checker chart) was just fitted in a longitudinal position of an image portion.

These photographed films were subjected to the same processing as described in Example 1 and printed onto color paper following the same procedures as in Example 1.

Consequently, it was confirmed that the resultant prints had high image qualities equivalent to those of the prints obtained from the same samples of Group II in Example 1.

It was also possible to miniaturize the cartridge and hence the camera by processing the films to have a width of 24 mm.

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## Claims

 A silver halide color photographic light-sensitive material having at least one hydrophilic colloid layer containing a compound represented by Formula (A) below on a support, characterized in that said support comprises a belt-like polyester base, not more than four perforations are formed per frame in one or both of side edge portions of said polyester base, the area of an imaging area is 3.0 cm<sup>2</sup> to 7.0

one or both of side edge portions of said polyester base, the area of an imaging area is 3.0 cm<sup>2</sup> to 7.0 cm<sup>2</sup>, and the aspect ratio of the imaging area is 1.40 to 2.50:

Formula (A) A-(Time)<sub>n</sub>-W

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wherein A represents a group capable of releasing  $(Time)_n$ -W upon reacting with an oxidized form of a color developing agent, Time represents a timing group, W represents a group which exhibits a development inhibiting effect after released from  $(Time)_n$ -W, and n represents 1, 2, or 3.

- **25 2.** A material according to claim 1, characterized in that said support is heat-treated at a temperature lower by 30 ° C to 50 ° C than the glass transition temperature of said support.
  - 3. A material according to claim 1, characterized in that a thickness of said support is 40  $\mu$ m to 300  $\mu$ m.
- 30 4. A material according to claim 1, characterized in that said support contains dyes.
  - 5. A material according to claim 1, characterized in that said material has a back layer which contains a fine grain of at least one crystalline metal oxide selected from the group consisting of ZnO, TiO<sub>3</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO, BaO, and MoO<sub>3</sub>, or fine grain of a composite oxide of these oxides.
- 35
- 6. A material according to claim 1, characterized in that a ratio of the total area of said perforations is 5% or less with respect to the area of one frame.
- A material according to claim 1, characterized in that said compound represented by Formula (A) is contained in a light-sensitive silver halide emulsion layer, and an addition amount of said compound is 0.01 to 20 mol% with respect to an amount of a silver halide in that layer.
- 8. A material according to claim 1, characterized in that said compound represented by Formula (A) is contained in a non-light-sensitive layer, and an addition amount of said compound is 0.01 to 20 mol%
   with respect to an amount of a silver halide in a silver halide emulsion layer closet to said non-light-sensitive layer.
  - **9.** A material according to claim 1, characterized in that said support is made from polyethylene-2,6-dinaphthalate.
- 50
- **10.** A material according to claim 9, characterized in that said support is heat-treated at a temperature lower by 30 ° C to 50 ° C than the glass transition temperature of polyethylene-2,6-dinaphthalate.

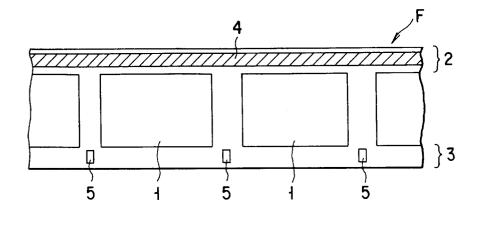


FIG. 1

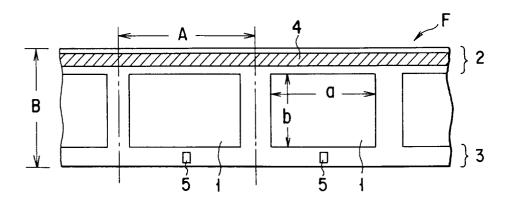
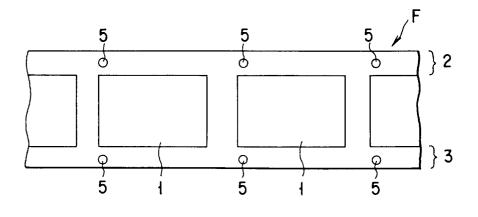
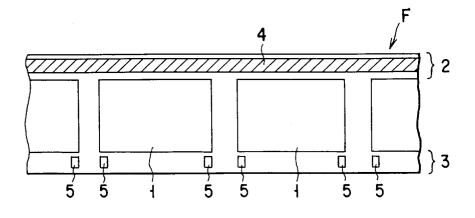


FIG. 2



F | G. 3



F I G. 4

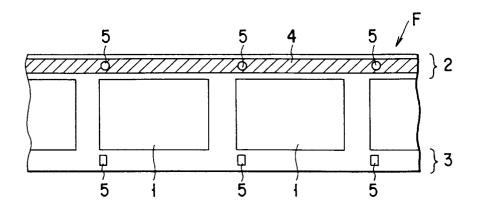


FIG. 5

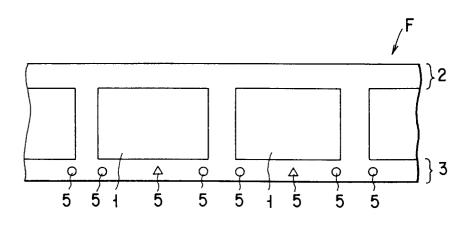


FIG. 6

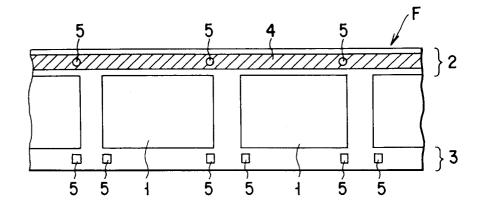
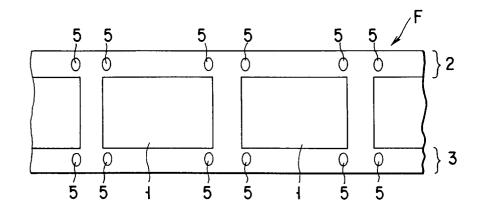
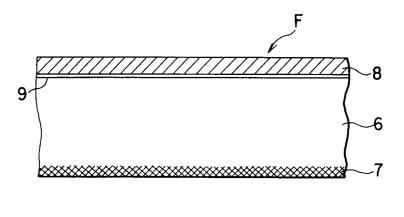


FIG. 7



F I G. 8



F | G. 9



European Patent Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 11 4872

	DOCUMENTS CONSIL	DERED TO BE RELEV	VANT			
Category	Citation of document with inc of relevant pass		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
Y	EP-A-0 476 327 (FUJI * page 4, line 21 - * page 4, line 44 - * page 13, line 24 - * page 30, line 53 - * page 76; example C * figure 1 *	line 26 * line 47 * line 45 * line 55 *	1-10	G03C1/795 G03C1/765 G03C1/81		
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				TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
				G03C		
	The present search report has been present search	n drawn up for all claims Date of campletion of the sea	rch	Examiner		
THE HAGUE 28 OCT		28 OCTOBER 1993		MAGRIZOS S.		
X : part Y : part doc A : tech	CATEGORY OF CITED DOCUMEN' ticularly relevant if taken alone ticularly relevant if combined with anot ument of the same category mological background -written disclosure	E : earlier pa after the ber D : document L : document		lished on, or		