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US-A- 3 052 543
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Proprietor : **FUJI PHOTO FILM CO., LTD.**
210 Nakanuma
Minami-Ashigara-shi
Kanagawa 250-01 (JP)

Proprietor : **TORAY INDUSTRIES,**
INCORPORATED
4845, Mishima-shi
Shizuoka (JP)

Inventor : **Satake, Seimi**
210, Nakanuma
Minami Ashigara-shi Kanagawa (JP)
Inventor : **Shibahara, Yoshihiko**
210, Nakanuma
Minami Ashigara-shi Kanagawa (JP)
Inventor : **Ueda, Toshiaki**
4845, Mishima-shi
Shizuoka (JP)
Inventor : **Kida, Kenji**
4845, Mishima-shi
Shizuoka (JP)

Representative : **Patentanwälte Dr. Solf & Zapf**
Candidplatz 15
D-81543 München (DE)

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Description**FIELD OF THE INVENTION**

5 This invention relates to a photographic light-sensitive material and, more particularly, to a photographic light-sensitive material which comprises a support of a polyester material and which has a light transparency and excellent curl-extinguishing properties after development processing, and these properties are independent of environment with a lapse of time.

BACKGROUND OF THE INVENTION

Photographic light-sensitive materials are generally produced by coating at least one photographic light-sensitive layer on a plastic film support. As the plastic film, fiber type polymers represented by triacetyl cellulose (hereinafter abbreviated as "TAC") and polyester type polymers represented by polyethylene terephthalate (hereinafter abbreviated as "PET") are generally used.

PET has conventionally been considered to substitute for TAC due to its excellent productivity, mechanical strength and dimensional stability. In the rolled state widely employed for photographic light-sensitive materials, however, PET has a strong tendency to retain the curl from being in the rolled state, and hence its handling properties after development processing are so poor that the scope of its application has been limited in spite of the above-described excellent properties.

Photographic light-sensitive materials generally include sheet form types such as X-ray films, plate-making films and cut films and roll films. Typical examples of the roll films are color or black-and-white negative-working films of 35 mm or less in width retained in a cartridge and adapted to be loaded in ordinary cameras for taking photographs.

On the other hand, the greatest aspect as a photographic support of TAC films mainly used for roll films is that they are optically non-anisotropic and have a high transparency. In addition, they have another excellent aspect. That is, they possess excellent properties as to curl-extinguishing after development processing. Since TAC films have comparatively high water-absorbing properties for plastic films due to their molecular structure, the molecular chain is fluidized upon absorption of water during development processing and the curling tendency imparted by being kept in a rolled state as roll film for a long time is extinguished as a result of rearrangement of the molecular chain which had been set after being rolled for a long time. With photographic light-sensitive materials using films which do not have the curling tendency-extinguishing properties of TAC films, however, there arise problems of, for example, flaw formation, unfocusing, and jamming upon conveying when used in a rolled state, for example, in the printing step of forming an image on a photographic printing paper after development.

Recently, acceleration of film-conveying speed upon photographing, enhancement of photographing magnification, and reduction in size of photographing apparatuses have become remarkable. In such situations, supports for photographic light-sensitive materials are required to have enough strength, dimensional stability, reduction in film thickness, to meet these new advances.

However, the above-described TAC provides only a fragile film when formed into film due to its rigid molecular structure and cannot be used in for these advances. Additionally, PET films cannot be used as a roll film where the curling tendency is problematical, in spite of their excellent mechanical properties. Thus, considerable improvement in PET films is greatly desired.

US-A-4,217,441 and 4,241,170 disclose that a PET film modified by reacting with a certain specific compound is employed as a support for a photographic material. In this case, however, there arise problems that the film becomes whitening by a processing and a lapse of time, and the transparency of the film is diminished. Therefore, further improvements for the transparency of the film have been desired.

US-A-3052 543 discloses a photographic material comprising a specific support film having thereon at least one layer of a copolymer of vinylidene chloride, an acrylic ester and itaconic acid and at least one layer of a water-permeable colloid having protective colloid properties. The support film comprises a polyester film formed by reacting a specific dicarboxylic acid (or a derivative thereof) with a specific dihydroxy compound and a specific metal sulfonate.

SUMMARY OF THE INVENTION

55 Therefore, an object of the present invention is to provide a photographic light-sensitive material which comprises a polyester film support having a high transparency and excellent mechanical properties, and which has excellent curl-extinguishing properties after development processing.

The object of the present invention can be attained by a photographic light-sensitive material which comprises a polyester film support having provided thereon at least one light-sensitive silver halide emulsion layer, said polyester film having a haze of up to 3%, a water content of from 0.5 wt.-% to 5.0 wt.-%, a curl-extinguishing ratio to 50% or more, and containing as predominant constituents terephthalic acid component and a glycol component, said polyester film further comprising an aliphatic dicarboxylic acid component having 4 to 20 carbon atoms as a copolymerization component in an amount of from 3 to 25 mol% based on the terephthalic acid component, wherein the haze is measured in accordance with ASTM D1003-52 after heat treatment of the film at a temperature of 150°C for ten minutes, the water content is measured after first moisture-conditioning the film under conditions of 23°C and 30% RH for three hours, next dipping the film in distilled water at 23°C for fifteen minutes and then measuring the water content using a micromoisture meter at a drying temperature of 150°C, and the curl-extinguishing ratio is measured after first dipping the film in distilled water at 40°C for fifteen minutes, and then drying for three minutes in air in a thermostatic chamber maintained at 55°C while applying a load of 50g.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, the water content of polyester film is measured by moisture-conditioning the film under the conditions of 23°C, 30% RH and 3 hours, dipping the film in 23°C distilled water for 15 minutes, and then using a micromoisture meter (for example, model CA-02, made by Mitsubishi Chemical Industries, Ltd.) at a drying temperature of 150°C.

In the present invention, the term "polyester" means a polyester containing as predominant constituents a terephthalic acid component and a glycol. Examples of the terephthalic acid component include terephthalic acid and isophthalic acid, and examples of the glycol include ethylene glycol, propylene glycol, butanediol, neopentyl glycol, 1,4-cyclohexanediol and diethylene glycol. Of the polyester films comprising these components, polyethylene terephthalate (PET) is most convenient from the standpoint of availability, and hence descriptions hereinafter will be made by reference to PET.

Copolymerized PET films preferably used in the present invention comprise copolymerized PET films containing a metal sulfonate-containing aromatic dicarboxylic acid component as a copolymerizable component.

Specific examples of the metal sulfonate-containing aromatic dicarboxylic acid include 5-sodium sulfisophthalic acid, 2-sodium sulfoterephthalic acid, 4-sodium sulfophthalic acid, 4-sodium sulfo-2,6-naphthalenedicarboxylic acid and compounds wherein sodium of the above-described compounds is replaced by another metal (for example, potassium or lithium). The copolymerization proportion of the metal sulfonate-containing aromatic dicarboxylic acid component is preferably about 2 to 15 mol%, particularly preferably about 4 to 10 mol%, based on the aromatic dibasic acid component, e.g., the terephthalic acid component.

For copolymerization an aliphatic dicarboxylic acid component containing 4 to 20 carbon atoms in the copolymerized PET film is used in view of transparency, particularly depression of whitening and enhancement of bending resistance of the copolymerized PET film.

As specific examples of the aliphatic dicarboxylic acid component containing 4 to 20 carbon atoms, there are illustrated succinic acid, adipic acid, sebacic acid, with adipic acid being particularly preferable. The copolymerization proportion of the aliphatic dicarboxylic acid component containing 4 to 20 carbon atoms is 3 to 25 mol%, preferably 5 to 20 mol%, based on the terephthalic acid component.

Additionally, in the polyester film of the present invention, other acid components or glycol components may further be copolymerized in a small proportion so as not to inhibit transparency and mechanical properties. For example, polyalkylene glycol, particularly polyethylene glycol, may be copolymerized in a proportion of 0 to 10 wt% based on the amount of the polyester produced. The polyalkylene glycols to be used for the above-described objects preferably have a molecular weight of about 600 to 10,000. The polyester film of the present invention preferably comprises a polymer having an intrinsic viscosity of about 0.5 to 0.9 measured in o-chlorophenol at 25°C.

Further, various additives may be incorporated in the polyester film of the present invention. In using a polyester film as a support for a photographic light-sensitive material, one of the problems is a problem of light piping due to a high refractive index of the support. As photographic supports, there are generally used triacetyl cellulose (TAC) and polyester type polymers represented by PET. One of the great optical differences between TAC and PET is the refractive index. PET has a refractive index of about 1.6, whereas TAC has a smaller refractive index of 1.5. On the other hand, gelatin mainly used in the subbing layer and photographic emulsion layer has a refractive index of 1.50 to 1.55. Thus, the ratio of the refractive index of gelatin to that of PET is 1.5/1.6, which is smaller than 1. Therefore, when light streams through a film edge, the light is liable to be reflected at the interface between the base and emulsion layer, thus polyester type films are liable to cause so-called light piping.

As techniques for avoiding the light piping phenomenon, there are known, for example, a technique of incorporating inert inorganic particles or the like in the film and a technique of adding a dye. A technique of preventing light piping preferably employed in the present invention is the technique of adding a dye which does not seriously raise film haze.

5 Dyes to be used for dyeing film are not particularly limited, but the tone is preferably gray in view of the general properties of light-sensitive materials. Dyes to be employed are preferably those which have an excellent heat resistance in a temperature region where the polyester film is formed and have an excellent compatibility with polyester.

From the above-described point of view, dyes commercially available as dyes for polyesters such as Diaresin (made by Mitsubishi Chemical Industries, Ltd) and Kayaset (made by Nippon Kayaku K.K.) may be used for attaining the above-described object.

As to dyeing density, at least a color density in the visible region of 0.01 measured by a color densitometer (made by Macbeth Co.) is necessary, with 0.03 or more being more preferable.

To the polyester film in accordance with the present invention may be imparted lubricating properties as the application demands. There are no limits as to techniques for imparting lubricating properties, but a technique of kneading an inert inorganic compound into the film or a technique of coating a surfactant is employed in general.

The inert inorganic particles are illustrated by SiO_2 , TiO_2 , BaSO_4 , CaCO_3 , talc, kaolin. In addition, a technique of adding the inert particles to the polyester-synthesizing reaction system to impart lubricating properties by the external particle system and a technique of precipitating catalyst or the like having been added upon the polymerization reaction of polyester to impart lubricating properties by the internal particle system are also employable.

Since transparency is an important factor as a support for photographic light-sensitive materials, SiO_2 having a comparatively approximate refractive index to that of polyester film is preferably selected as the external particle system, or an internal particle system capable of precipitating particles of a comparatively small particle size is preferably selected as the internal particle system, which, however, do not limit the technique of imparting lubricating properties.

Further, in the case of imparting lubricating properties by the kneading technique, it is also preferable to laminate a layer which functions to impart transparency to the film. As the technique for lamination, there is illustrated a coextruding process using a plurality of extruders and a feed block or multi-manifold die.

In the present invention, precipitation of low-polymerized product upon thermal treatment for forming a subbing layer sometimes takes place with some copolymerization ratio. In such a situation, it is possible to laminate an ordinary polyester layer on at least one side of the support. For this lamination, too, the co-extruding process is employed as an effective technique.

35 Starting polymers for the copolymerized PET film of the present invention can be synthesized according to conventionally known processes for producing polyesters. For example, copolymerized PET can be obtained by directly subjecting the dibasic acid component and the glycol component to an esterification reaction at a temperature of 200°C to 270°C and removing a theoretical amount of water or, by using a lower alkyl ester as the dibasic acid component, and conducting an ester interchange reaction between the dibasic acid component and the glycol component at a temperature of 100°C to 250°C and removing a theoretical amount of lower alcohol to obtain a glycol ester of the dibasic acid or a low molecular weight polymer. Then, the product obtained is heated at a temperature of 200°C to 300°C under a pressure gradually reduced to about 133 Pa (1 Torr) to remove excess glycol component. In this situation, an ester interchange reaction catalyst or a polymerization reaction catalyst described in US-A-2,647,885 and 2,739,957, GB-B-742,196 and 770,531 may be used, or a heat resistant stabilizing agent described in the above patents may be added thereto.

The thus-obtained copolymerized PET is generally granulated, dried, melt-extruded to form an unstretched film sheet, then biaxially stretched and heat-treated to obtain the end film.

The biaxial stretching may be conducted successively in the order of longitudinal direction and transverse direction or in the reverse order, or simultaneously in two directions. The stretching ratio is not particularly limited, but is usually 2.0 to 5.0 times. Restretching in the transverse or longitudinal direction may be conducted after stretching in the transverse or longitudinal direction.

As a drying technique in the present invention employed before melt-extrusion, a vacuum drying technique or a dehumidification-drying technique is preferable.

Stretching temperatures in the present invention are desirably from 70 to 100°C upon longitudinal stretching and from 80 to 160°C upon transverse stretching.

Heat-setting temperatures are from 150 to 210°C, particularly preferably from 60 to 200°C.

The thickness of the copolymerized PET film to be used in the present invention may properly be determined depending upon the end-use of photographic film, and is desirably from 25 to 250 μm , more desirably

from 40 to 150 μm .

The copolymerization formulation in the present invention does not spoil the excellent transparency and mechanical strength which PET essentially possesses, and provides a film haze of up to 3%, a breaking strength of from 8 to 25 kg/mm², an initial modulus of from 200 to 500 kg/mm², and a tear strength at a thickness of 120 μm of not less than 30 g. If the strength is less than the above-described range, the excellent mechanical strength which PET essentially possesses is spoiled and, thus, the superiority over TAC is lost.

In the present invention, transparency, breaking strength, initial modulus and tear strength are measured as follows.

Transparency

Haze of a film is measured according to ASTM D1003-52 after a heat treatment of the film at a temperature of 150°C for 10 minutes. This heat treatment is usually subjected to a film support at a coating step of a photographic layer.

Breaking Strength and Initial Modulus

A sample of 10 mm in width and 100 mm in length is subjected to measurement according to JIS Z1702-1976 employing a pulling rate of 300 mm/min for measuring breaking strength and 20 mm/min for measuring initial modulus.

The polyester film support to be used in the present invention has excellent curling tendency-extinguishing properties after development processing (hereinafter referred to as curl-extinguishing ratio). In the present invention, the curl-extinguishing ratio measured according to the following method is 50% or more, preferably 80% or more.

Measurement of Curl-Extinguishing Ratio

A sample of 12 cm $\times$ 35 cm in size is wound around a core of 10 mm in diameter and is kept under the conditions of 60°C $\times$ 30% RH $\times$ 72 hrs. Then, it is unwound from the core, dipped in 40°C distilled water for 15 minutes, and dried for 3 minutes in a 55°C air thermostatic chamber while applying a load of 50 g. The length of the thus-treated sample is measured in a perpendicularly suspended state to evaluate the degree of restoration to the original length of 12 cm.

The copolymerized PET film to be used in the present invention has a better adhesiveness to various coating layers such as emulsion layers than conventional PET films.

The polyester film to be used in the present invention may, if necessary, be previously subjected to corona discharge treatment, treatment with a chemical solution or flame treatment. Of these surface treatments, corona discharge treatment is most preferably used in the present invention, since it causes less precipitation of low-polymerized product on the film surface.

The polyester support to be used in the present invention preferably has a subbing layer for enhancing adhesion to a photographic layer such as a light-sensitive layer to be coated thereon.

As the subbing layer, there are illustrated a subbing layer using a polymer latex composed of a styrene-butadiene type copolymer or a vinylidene chloride copolymer and a subbing layer using a hydrophilic binder such as gelatin.

The subbing layer using a hydrophilic binder is preferably used as the subbing layer in the present invention.

As the hydrophilic binder to be used in the present invention, there are illustrated, for example, water-soluble polymers, cellulose esters, latex polymers and water-soluble polyesters. The water-soluble polymers include gelatin, gelatin derivatives, casein, agar-agar, sodium alginate, starch, polyvinyl alcohol, polyacrylic acid copolymers and maleic anhydride copolymers, and the cellulose esters include carboxymethyl cellulose and hydroxyethyl cellulose. The latex polymers include vinyl chloride-containing copolymers, vinylidene chloride-containing copolymers, acrylic ester-containing copolymers, vinyl acetate-containing copolymers and butadiene-containing copolymers. Of these, gelatin is most preferable.

As compounds capable of swelling the support to be used in the present invention, there are illustrated, for example, resorcin, chlororesorcin, methylresorcin, o-cresol, m-cresol, p-cresol, phenol, o-chlorophenol, p-chlorophenol, dichlorophenol, trichlorophenol, monochloroacetic acid, dichloroacetic acid, trifluoroacetic acid, and chloral hydrate. Of these, resorcin and p-chlorophenol are preferable.

Various gelatin hardeners may be used in the subbing layer of the present invention.

As the gelatin hardeners, there are illustrated, for example, chromium salts (e.g., chromium alum), alde-

hydes (e.g., formaldehyde and glutaraldehyde), isocyanates, active halogen compounds (e.g., 2,4-dichloro-6-hydroxy-s-triazine) and epichlorohydrin resin.

The subbing layer to be used in the present invention may contain fine particles of an inorganic substance such as SiO_2 or TiO_2 or fine particles (1 to 10 μm) of polymethyl methacrylate copolymer as matting agents.

The subbing layer to be used in the present invention may be coated according to a generally well known coating process such as a dip coating process, an air knife coating process, a curtain coating process, a wire bar coating process, a gravure coating process, or an extrusion coating process.

The light-sensitive material of the present invention may have light-insensitive layers such as an anti-halation layer, an interlayer, a backing layer and a surface protecting layer in addition to light-sensitive layers.

The binder for the backing layer may be a hydrophobic polymer, or may be a hydrophilic polymer as used for the subbing layer.

The backing layer of the light-sensitive material in accordance with the present invention may contain an antistatic agent, a slipping agent, a matting agent, a surfactant or a dye. The antistatic agents to be used in the present invention are not particularly limited and are, for example, anionic high molecular weight electrolytes such as high molecular weight polymers containing carboxylic acid groups, carboxylic acid salt groups or sulfonic acid groups (e.g., high polymers as described in JP-A-48-22017 (the term "JP-A" as used herein refers to a "published unexamined Japanese patent application"), JP-B-46-24159 (the term "JP-B" as used herein refers to an "examined Japanese patent publication"), JP-A-51-30725, JP-A-51-129216, JP-A-55-95942) and cationic high polymers as described in JP-A-49-121523, JP-A-48-91165, JP-B-49-24582, etc. Ionic surfactants also include anionic and cationic surfactants and are exemplified by those which are described in JP-A-49-85826, JP-A-49-33630, US-A-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 antistatic agents for the backing layer of the present invention are fine particles of at least one crystalline metal oxide selected from among ZnO , TiO_2 , SnO_2 , Al_2O_3 , In_2O_3 , SiO_2 , MgO , BaO and MoO_3 , or a composite oxide thereof.

Fine particles of the conductive crystalline oxides or their composite oxides to be used in the present invention have a volume resistivity of up to $10^7 \Omega\cdot\text{cm}$, more preferably up to $10^5 \Omega\cdot\text{cm}$, and have a particle size of 0.01 to 0.7 μm , particularly preferably 0.02 to 0.5 μm .

Processes for producing the fine particles of the conductive crystalline metal oxides or their composite oxides to be used in the present invention are described in detail in JP-A-56-143430 (corresponding to US-A-4,495,276) and JP-A-60-258541. They can be easily produced firstly by producing fine particles of metal oxide through baking and heat-treating the particles in the presence of a different atom capable of improving conductivity; secondly by allowing a different metal capable of improving conductivity to coexist upon production of metal oxide fine particles through baking; or thirdly by reducing the oxygen concentration of the atmosphere upon production of metal oxide fine particles through baking to thereby introduce an oxygen deficiency. Examples of different atoms are: Al, In, for ZnO ; Nb, Ta, for TiO_2 ; and Sb, Nb, halogen atoms, for SnO_2 . The different atom is added in an amount of preferably 0.01 to 30 mol%, particularly preferably 0.1 to 10 mol%.

Photographic layers of the photographic light-sensitive material for the present invention are now described below. The most preferable examples of the photographic light-sensitive material in accordance with the present invention are silver halide photographic light-sensitive materials which are exemplified by silver halide color negative-working films, color positive-working films, color reversal films and black-and-white negative-working films.

The photographic emulsion to be used in the present invention can be prepared by the processes described in P. Glafkides, *Chimie et Physique Photographique* (Paul Montel, 1967), G.F. Duffin, *Photographic Emulsion Chemistry* (The Focal Press, 1966), V.L. Zelikman et al., *Making and Coating Photographic Emulsion* (The Focal Press, 1964). That is, any of an acidic process, a neutral process and an ammoniacal process may be used. As a manner of reacting a soluble silver salt with a soluble halide salt, any of one side mixing, simultaneous mixing, and combinations thereof may be employed.

A process of forming silver halide grains in the presence of excess silver ion (called reverse mixing process) can be employed as well. As one type of the simultaneous mixing, a process called a controlled double jet process wherein the pAg in a liquid phase in which silver halide is formed is kept constant can be employed. This process provides a silver halide emulsion containing silver halide grains of regular crystal form having an approximately uniform grain size.

Two or more silver halide emulsions having been separately prepared may be mixed for use.

During formation or physical ripening of silver halide grains, cadmium salts, zinc salts, lead salts, thallium salts, iridium salts or the complex salts thereof, rhodium salts or the complex salts thereof, iron salts or the complex salts thereof, may be allowed to coexist.

As a binder or protective colloid for photographic emulsions, gelatin is advantageously used. However,

other hydrophilic colloids can be used as well. For example, proteins such as gelatin derivatives, graft polymers between gelatin and other high molecular weight polymers, albumin, casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate; sugar derivatives such as sodium alginate, starch derivative; and various synthetic macromolecular substances such as homopolymers or copolymers (e.g., polyvinyl alcohol, partially acetalized polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl imidazole, polyvinyl pyrazole) can be used.

As gelatin, acid-processed gelatin or enzyme-processed gelatin as described in *Bull. Soc. Sci. Phot. Japan*, No. 16, p. 30 (1966) may be used as well as lime-processed gelatin, and a gelatin hydrolyzate or an enzyme-decomposed product can also be used. As gelatin derivatives, those obtained by reacting gelatin with various compounds such as acid halides, acid anhydrides, isocyanates, bromoacetic acid, alkanesultones, vinyl-sulfonamides, maleimide compounds, polyalkylene oxides, epoxy compounds or the like can be used. Specific examples thereof are described in US-A-2,614,928, 3,123,945, 3,186,846, 3,312,553, GB-B-861,414, 1,033,189, and 1,005,784, JP-B-42-26845.

As the aforesaid gelatin graft polymers, products prepared by grafting to gelatin a homo- or copolymer of a vinyl monomer such as acrylic acid, methacrylic acid, esters or amides thereof, acrylonitrile, styrene can be used. In particular, graft polymers between gelatin and a polymer having some compatibility with gelatin such as a polymer of acrylic acid, methacrylic acid, acrylamide, methacrylamide, hydroxyalkyl methacrylate are preferable. Examples of these are described in US-A-2,763,625, 2,831,767, 2,956,884.

Typical synthetic high molecular weight substances are those described in, for example, DE-A-2,312,708, US-A-3,620,751 and 3,879,205 and JP-B-43-7561.

In the photographic emulsion to be used in the present invention, various compounds for preventing fog or stabilizing the photographic properties during production steps, storage, or photographic processing of the light-sensitive material may be incorporated. That is, many compounds known as antifogging or stabilizing agents such as azoles (e.g., benzothiazolium salts, nitroindazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptotriazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, mercaptotetrazoles (particularly, 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; thioketo compounds (e.g., oxazoline-thione); azaindenes (e.g., triazaindenes, tetraazaindenes (particularly, 4-hydroxy-substituted 1,3,3a,7-tetraazaindenes,); pentaazaindenes); benzenethiosulfonic acid; benzenesulfonic acid; benzenesulfonamide; may be added. For example, those described in US-A-3,954,474 and 3,982,947, JP-B-52-28660, may be used.

The photographic emulsion layer of the photographic light-sensitive material in accordance with the present invention may contain a polyalkylene oxide or its ether, ester or amide derivative, a thioether compound, a thiomorpholine, a quaternary ammonium salt compound, a urethane derivative, a urea derivative, an imidazole derivative, a 3-pyrazolidone, etc., for the purpose of enhancing sensitivity or contrast or for accelerating development. For example, those described in US-A-2,400,532, 2,423,549, 2,716,062, 3,617,280, 3,772,021 and 3,808,003, GB-B-1,488,991, may be used.

The photographic emulsion used in the present invention may be spectrally sensitized with methine dyes. Suitable dyes include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are those belonging to cyanine dyes, merocyanine dyes, and complex merocyanine dyes. These dyes may contain as a basic heterocyclic nucleus any of the nuclei usually used for cyanine dyes.

That is, there can be contained a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, a pyridine nucleus; nuclei wherein an alicyclic hydrocarbon ring or rings are fused to these nuclei; and nuclei wherein an aromatic hydrocarbon ring or rings are fused to these nuclei, i.e., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus. These nuclei may be substituted on the carbon atom or atoms thereof.

Merocyanine dyes or complex merocyanine dyes contain, as a ketomethylene structure-containing nucleus, a 5- or 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus and a thiobarbituric acid nucleus.

Useful sensitizing dyes are described in, for example, DE-C-929,080, US-A-2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,959, 3,672,897, 3,694,217, 4,025,349, 4,046,572, GB-B-1,242,588, JP-B-44-14030 and JP-B-52-24844.

These sensitizing dyes may be used alone or in combination. Combinations of sensitizing dyes are often used for attaining, in particular, supersensitization. Typical examples thereof are described in US-A-2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428,

3,703,377, 3,769,301, 3,814,609, 3,837,862, 4,026,707 GB-B-1,344,281 and 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618, and JP-A-52-109925.

Dyes which themselves do not show a spectrally sensitizing action or materials which do not substantially absorb visible light, showing supersensitivity, may be incorporated in the emulsion together with the sensitizing dyes. For example, aminostilbenes substituted by a nitrogen-containing heterocyclic group (for example, those described in US-A-2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (for example, those described in US-A-3,743,510), cadmium salts, azaindene compounds, etc., may be incorporated. Combinations described in US-A-3,615,613, 3,615,641, 3,617,295, 3,635,721 are particularly useful.

The light-sensitive material of the present invention may contain water-soluble dyes as filter dyes or for various purposes like antiirradiation. Such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes, and azo dyes. Of these, oxonol dyes, hemioxonol dyes, and merocyanine dyes are useful. Specific examples of usable dyes are described in GB-B-584,609 and 1,177,429, JP-A-48-85130, JP-A-49-99620, JP-A-49-114420, JP-A-52-108115, US-A-2,274,782, 2,533,472, 2,956,879, 3,148,187, 3,177,078, 3,247,127, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 4,071,312, and 4,070,352.

In the light-sensitive material obtained according to the present invention, photographic emulsion layers and other hydrophilic colloidal layers may contain fluorescent brightening agents of stilbenes, triazines, oxazoles, coumarins, etc. These agents may be of a water-soluble type or water-insoluble type, with the latter being used in the form of a dispersion. Specific examples of the fluorescent brightening agents are described in US-A-2,632,701, 3,269,840, 3,359,102, GB-B-852,075 and 1,319,763.

In the practice of the present invention, the following known dye stabilizers can be used in combination. The color image stabilizing agents to be used in the present invention may be used alone or in combinations of two or more. The known dye stabilizers include, for example, hydroquinone derivatives described in US-A-2,360,290, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,659, 2,732,300, 2,735,765, 2,710,801, 2,816,028, GB-B-1,363,921, gallic acid derivatives described in US-A-3,457,079, 3,069,262 p-alkoxyphenols described in US-A-2,735,765 and 3,698,909, JP-B-49-20977, JP-B-52-6623, p-hydroxyphenols described in US-A-3,432,300, 3,573,050, 3,574,627, 3,764,337, JP-A-52-35633, JP-A-52-147434, JP-A-52-152225, bisphenols described in US-A-3,700,455.

The light-sensitive material prepared by the present invention may contain hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives, ascorbic acid derivatives, as color fog preventing agents. Specific examples thereof are described in US-A-2,360,290, 2,336,327, 2,403,721, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,659, 2,732,300, 2,735,765, JP-A-50-92988, JP-A-50-92989, JP-A-50-93928, JP-A-50-110337, JP-A-52-146235, JP-B-50-23813, etc.

The present invention may be applied to a multilayered multicolor photographic material having at least two light-sensitive layers different in spectral sensitivity. Multilayered color photographic materials usually comprise a support having provided thereon at least one red-sensitive emulsion layer, at least one green-sensitive emulsion layer and at least one blue-sensitive emulsion layer. The order of these layers may be optionally selected as the case demands. Usually, the red-sensitive emulsion layer is associated with a cyan-forming coupler, the green-sensitive emulsion layer is associated with a magenta-forming coupler, and the blue-sensitive emulsion layer is associated with a yellow-forming coupler, though different combinations are possible in some cases.

The most preferable light-sensitive materials of the present invention are rolled color negative films for photographing use.

Known color couplers may preferably be used in the color negative-working films of the present invention.

That is, they may contain compounds capable of forming dyes by the reaction with an oxidation product of an aromatic amine (usually primary amine) developing agent (hereinafter abbreviated as "couplers"). As the couplers, nondiffusible couplers having a hydrophobic group called a ballast group in the molecule are desirable. The couplers may be of either 4-equivalent type or 2-equivalent type based on silver ion. Colored couplers having color-correcting effects or couplers capable of releasing a development inhibitor upon development (called DIR couplers) may also be incorporated. Couplers may be those which form a colorless coupling reaction product.

As yellow color-forming couplers, known open chain ketomethylene couplers may be used. Of these, benzoylacetyl type and pivaloylacetyl type compounds are advantageous. Specific examples of usable yellow color-forming couplers are those described in US-A-2,875,057, 3,265,506, 3,408,194, 3,551,155, 3,582,322, 3,725,072, 3,891,445, DE-C-1,547,868, DE-A-2,219,917, 2,261,361, 2,414,006, GB-B-1,425,020, JP-B-51-10783, JP-A-47-26133, JP-A-48-73147, JP-A-51-102636, JP-A-50-6341, JP-A-50-123342, JP-A-50-130442, JP-A-51-21827, JP-A-50-87650, JP-A-52-82424, JP-A-52-115219.

As magenta color-forming couplers, pyrazolone type compounds, indazolone type compounds, cyanoacetyl compounds may be used, with pyrazolone type compounds being particularly advantageous. Specific

examples of usable magenta color-forming couplers are described in US-A-2,600,788, 2,983,608, 3,062,653, 3,127,269, 3,311,476, 3,419,391, 3,519,429, 3,558,319, 3,582,322, 3,615,506, 3,834,908, 3,891,445, DE-C-1,810,464, DE-A-2,408,665, 2,417,945, 2,418,959, 2,424,467, JP-B-40-6031, JP-A-51-20826, JP-A-52-58922, JP-A-49-129538, JP-A-49-74027, JP-A-50-159336, JP-A-52-42121, JP-A-49-74028, JP-A-50-60233, JP-A-51-26541, JP-A-53-55122.

As cyan color-forming couplers, phenolic compounds, naphtholic compounds, may be used. Specific examples thereof are those described in US-A-2,369,929, 2,434,272, 2,474,293, 2,521,908, 2,895,826, 3,034,892, 3,311,476, 3,458,315, 3,476,563, 3,583,971, 3,591,383, 3,767,411, 4,004,929, DE-A-2,414,830 and 2,454,329, JP-A-48-59838, JP-A-51-26034, JP-A-48-5055, JP-A-51-146828, JP-A-52-69624, JP-A-52-90932.

As colored couplers, those which are described in, for example, US-A-3,476,560, 2,521,903, 3,034,892, JP-B-44-2016, JP-B-38-22335, JP-B-42-11304, JP-B-44-32461, JP-A-51-26034, JP-A-52-42121, DE-A-2,418,959 may be used.

As DIR couplers, those which are described in, for example, US-A-3,227,554, 3,617,291, 3,701,783, 3,790,384, 3,632,345, DE-A-2,414,006, 2,454,301, 2,454,329, GB-B-953,454, JP-A-52-69624, JP-A-49-122335, JP-B-51-16141, may be used.

Compounds capable of releasing a development inhibitor upon development may be incorporated in the light-sensitive material in addition to the DIR couplers, and those described in, for example, US-A-3,297,445, 3,379,529, DE-A-241,794, JP-A-52-15271, JP-A-53-9116 may be used.

The above-described couplers may be used in combinations of two or more in one and the same layer, or the same compound may be used in two or more different layers.

These couplers are added to a photographic emulsion layer in an amount of 2×10^{-3} mol to 5×10^{-1} mol, preferably 1×10^{-2} mol to 5×10^{-1} mol, per mol of silver contained in the emulsion layer.

The couplers can be introduced into silver halide emulsion layers in a known manner described in, for example, US-A-2,322,027. For example, they are dissolved in an alkyl phthalate (e.g., dibutyl phthalate or dioctyl phthalate), a phosphoric ester (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, dioctylbutyl phosphate), a citric acid ester (e.g., tributyl acetylcitrate), a benzoic acid ester (e.g., octyl benzoate), an alkylamide (e.g., diethylaurylamide), a fatty acid ester (e.g., dibutoxyethyl succinate or dioctyl azelate) or in an organic solvent having a boiling point of about 30°C to about 150°C such as a lower alkyl acetate (e.g., ethyl acetate or butyl acetate), ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone, β -ethoxyethyl acetate, methyl cellosolve or the like, and the resulting solution is dispersed in a hydrophilic colloid. The above-described high boiling organic solvent and the low boiling organic solvent may be mixed for use.

A dispersing process using a polymer as described in JP-B-51-39853 and JP-A-51-59943 may also be employed.

With couplers having an acid group such as a carboxylic acid or a sulfonic acid group, they are introduced into a hydrophilic colloid as an alkaline aqueous solution.

The light-sensitive material prepared according to the present invention may contain in its hydrophilic colloidal layer an ultraviolet ray absorbent. For example, aryl group-substituted benzotriazole compounds (e.g., those described in US-A-3,533,794), 4-thiazolidone compounds (e.g., those described in US-A-3,314,794 and 3,352,681), benzophenone compounds (e.g., those described in JP-A-46-2784), cinnamic acid esters (e.g., those described in US-A-3,705,805 and 3,707,375), butadiene compounds (e.g., those described in US-A-4,045,229) or benzoxazole compounds (e.g., those described in US-A-3,700,455) may be used. Further, those which are described in US-A-3,499,762 and JP-A-54-48535 may be used. Ultraviolet ray-absorbing couplers (e.g., α -naphtholic cyan dye-forming couplers) or ultraviolet ray-absorbing polymers may also be used. These ultraviolet ray-absorbing agents may be mordanted to a specific layer or layers.

In photographic processing of the light-sensitive material of the present invention, any of known processes may be used. The processing temperature is usually selected between 18°C and 50°C. However, temperatures lower than 18°C or higher than 50°C may be employed.

Either of development processing forming only silver images (black-and-white photographic processing) or color photographic processing comprising dye image-forming development processing may be used depending upon the end use.

Color developer generally comprises an alkaline aqueous solution containing a color developing agent. As the color developing agent, known primary aromatic amines such as phenylenediamines (for example, 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N- β -methanesulfonamidoethylaniline, 4-amino-3-methyl-N-ethyl-N- β -methoxyethylaniline) may be used.

In addition, those described in L.F.A. Mason, Photographic Processing Chemistry (Focal Press, 1966), pp. 226 to 229, US-A-2,193,015, 2,592,364, JP-A-48-64933 may also be used.

The color developer may further contain pH buffers such as alkali metal sulfites, carbonates, borates and phosphates, development inhibitors or anti-foggants such as bromides, iodides and organic anti-foggants and, if necessary, may contain water softeners, preservatives such as hydroxylamine, organic solvents such as benzyl alcohol and diethylene glycol, development accelerators such as polyethylene glycol, quaternary ammonium salts, and amines, dye-forming couplers, competitive couplers, fogging agents such as sodium borohydride, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity-imparting agent, polycarboxylic acid type chelating agents described in US-A-4,083,723, antioxidants described in DE-A-2,622,950.

Color developed photographic emulsion layers are usually bleached. Bleaching may be conducted separately or simultaneously with fixing. As bleaching agents, compounds of polyvalent metals such as iron(III), cobalt(III), chromium(VI), copper(II), etc., peracids, quinones, nitroso compounds are used. For example, ferricyanides, dichromates, organic complex salts of iron(III) or cobalt(III) such as complex salts of aminopolycarboxylic acids (e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, 1,3-diamino-2-propanoltetraacetic acid) or organic acids (e.g., citric acid, tartaric acid, malic acid); persulfates and permanganates; nitrosophenol may be used. Couplers of the present invention show a large color-forming ability even in a bleaching solution or bleach-fixing solution containing iron(III) sodium ethylenediaminetetraacetate or iron(III) ammonium ethylenediaminetetraacetate, thus being advantageous in this point as well. Iron(III) ethylenediaminetetraacetate complex salts are useful in both an independent bleaching solution and a monobath bleach-fixing solution.

To the bleaching or bleach-fixing solution may be added various additives such as bleaching accelerators described in US-A-3,042,520, 3,241,966, JP-B-45-8506, JP-B-45-8836 and thiol compounds described in JP-A-53-65732.

The present invention is now illustrated in greater detail by reference to the following examples which, however, are not to be construed as limiting the present invention in any way. Unless otherwise specified, all percents, ratios are by weight.

EXAMPLE 1

(1) Preparation of Polyester Film

0.1 Part by weight of calcium acetate monohydrate and 0.03 part by weight of antimony trioxide were added to 100 parts by weight of dimethyl terephthalate, 70 parts by weight of ethylene glycol, 10 parts by weight of dimethyl 5-sodium sulfoisophthalate and 10 parts by weight of dimethyl adipate in a reactor equipped with a fractionating column, and an ester interchange reaction was conducted by gradually heating and removing methanol produced. After the temperature was reached to 230°C, the reaction was continued at this temperature until 38 parts by weight of methanol was distilled out. 0.05 Part by weight of trimethyl phosphate was added to the resulting product, and the mixture was transferred to a reactor equipped with a pressure-diminishing device and the temperature was gradually raised and the pressure was gradually reduced to finally 280°C and not more than 1 mm Hg, respectively, to conduct polymerization. Thus, copolymerized PET was obtained after the lapse of 3 hours from the start of the reduction of pressure. The intrinsic viscosity of the copolymerized PET was 0.65 measured in o-chlorophenol at 25°C.

The resulting copolymerized PET was dried at 130°C for 5 hours, then melt-extruded at 280°C to obtain an unstretched film. The film was then successively stretched in a longitudinal direction at 90°C with a stretching ratio of 3.5 times and then in a transverse direction at 95°C with a stretching ratio of 3.7 times, and heat-set at 200°C for 5 seconds to obtain a 50 µm thick biaxially stretched film. This film had a haze of 1.2%, a breaking strength of 12 kg/mm, and an initial modulus of 340 kg/mm, and had good transparency and mechanical properties.

Additionally, transparency, breaking strength and initial modulus were measured under the following conditions.

Transparency:

Haze of a sample film was measured according to ASTM D1003-52 after a heat treatment of the film at a temperature of 150°C for 10 minutes.

Breaking Strength and Initial Modulus:

A sample of 10 mm in width and 100 mm in length was subjected to measurement according to JIS Z1702-1976 employing a pulling rate of 300 mm/min for measuring breaking strength and 20 mm/min for measuring initial modulus.

(2) Measurement of Curl-Extinguishing Ratio:

The polyester film (50 μm thick) of the present invention prepared as described above, a commercially available PET film (50 μm thick) and a commercially available TAC film (125 μm thick) were subjected to measurement of water content according to the method of the present invention.

Further, curl-extinguishing ratio was measured in a manner described below to obtain the results shown in Table 1.

Method for Evaluating Curl-Extinguishing Degree

A sample film of 12 cm $\times$ 35 cm in size was wound around a core of 10 mm in diameter and was subjected to treatment at 60°C $\times$ 30% RH $\times$ 72 hr. Then, the film was unwound from the core, dipped in 40°C distilled water for 15 minutes, and dried for 3 minutes in a 55°C air thermostatic chamber while applying a load of 50 g. The length of the thus-treated sample was measured in a perpendicularly suspended state to evaluate the degree of restoration to the original length of 12 cm.

TABLE 1

<u>Sample</u>	<u>Water Content (wt%)</u>	<u>Dipping Treatment</u>	<u>Curl- Extinguishing Ratio (%)</u>
TAC (125 μm)	2.6	Treated	38
		Not treated	14
PET (50 μm)	0.4	Treated	16
		Not treated	16
Present Invention (50 μm)	0.7	Treated	98
		Not treated	20

As is clear from Table 1, it is seen that polyester film in accordance with the present invention having a water content of 0.7 wt% shows an extremely large curl-extinguishing ratio.

(3) Preparation of Photographic Light-Sensitive Material

(3-1) Coating of Subbing Layer:

A subbing layer of the following formulation was coated on each of the aforesaid polyester film and commercially available PET film after corona discharge treatment of both sides of them. The corona discharge treatment was conducted to a degree of 0.02 KVA $\cdot$ min/m².

Gelatin	3 g
Distilled Water	250 cm ³
Sodium-sulfo-di-2-ethylhexyl-succinate	0.05 g
Formaldehyde	0.02 g

(3-2) Coating of Backing Layer:

A backing layer of the following formulation was coated on one side of the subbed polyester films.

Preparation of a Dispersion of Tin Oxide-Antimony Oxide Composite

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 obtain a uniform solution. A 1 N sodium hydroxide aqueous solution was dropwise added to the solution until the pH of the solution became 3 to obtain a coprecipitate of colloidal stannic oxide and antimony oxide. The thus-obtained coprecipitate was allowed to stand at 50°C for 24 hours to obtain a reddish brown colloidal precipitate.

The reddish brown colloidal precipitate was separated by centrifugal separation. In order to remove excess ions, water was added to the precipitate, followed by centrifugal separation to wash with water. This washing procedure was repeated 3 times to remove excess ions.

200 parts by weight of the colloidal precipitate freed of excess ions was again dispersed in 1,500 parts by weight of water, and sprayed into a 600°C heated baking furnace to obtain a fine powder of a bluish tin oxide-antimony oxide composite having an average particle size of 0.2 μm . This fine powder had a specific resistance of 25 $\Omega\cdot\text{cm}$.

A mixture of 40 parts by weight of the above-described fine powder and 60 parts by weight of water was adjusted to 7.0 in pH and, after being roughly dispersed by a stirrer, the mixture was dispersed by a horizontal sand mill (trade name: Dyno mill made by WILLY A. BACHOFEN AG) until a residential time became 30 minutes.

Coating of Backing Layer

Formulation (A) shown below was coated in a dry thickness of 0.3 μm , and dried at 130°C for 30 seconds. Coating Solution (B) shown below was coated in a dry thickness of 0.1 μm and dried at 130°C for 2 minutes.

<u>Formulation (A):</u>	<u>parts by weight</u>
Dispersion of Conductive Fine Particles	10
Gelatin	1
Water	27
Methanol	60
Resorcin	2
Polyoxyethylene Nonylphenyl Ether	0.01

Coating Solution (B) for Forming Coating Layer

	<u>parts by weight</u>
Cellulose Triacetate	1
Acetone	70
Methanol	15
Dichloromethylene	10
p-Chlorophenol	4

(3-3) Coating of Photographic Layers:

Photographic layers as described below were provided on the side opposite to the backing layer-coated

side of the PET film used in the present invention and the commercially available PET film.

First Layer: Red-Sensitive Silver Halide Low Sensitive Layer

(1-a) Preparation of an Emulsion Solution for Forming Low Sensitive Emulsion Layer

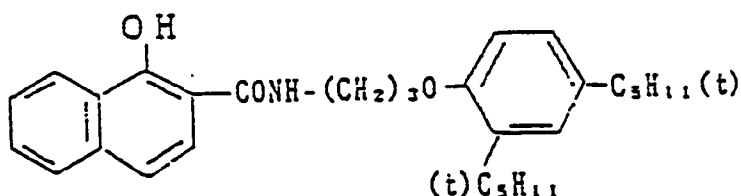
A silver bromoiodide emulsion containing 6 mol% iodide (average grain size: 0.6 μm ; containing 100 g of silver halide and 70 g of gelatin per kg of emulsion) was prepared in an ordinary manner. To 1 kg of this emulsion were added 180 cm^3 of a 0.1 wt% methanol solution of anhydro-5,5'-dichloro-9-ethyl-3,3'-di(3-sulfopropyl)-thiacarbocyanine hydroxide pyridinium salt as a red-sensitive sensitizer. Then, 20 cm^3 of a 5 wt% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine, 330 g of Cyan Coupler Emulsion (1) of the following formulation, and 20 g of Emulsion (2) were added thereto. Further, 50 cm^3 of a 2 wt% aqueous solution of 2-hydroxy-4,6-dichlorotriazine sodium salt were added thereto as a gelatin hardener to prepare an emulsion for forming a low sensitive emulsion.

Emulsion (1)

(i)	10 wt% Gelatin Aqueous Solution -	1,000 g
(ii)	Sodium p-Dodecylbenzenesulfonate	5 g
	Tricresyl Phosphate	60 cm^3
	Cyan Coupler (C-7)	70 g
	Ethyl Acetate	100 cm^3

A mixture of (ii) was made into a solution at 55°C, and the resulting solution was added to (i) previously heated to 55°C, followed by emulsification in a colloid mill.

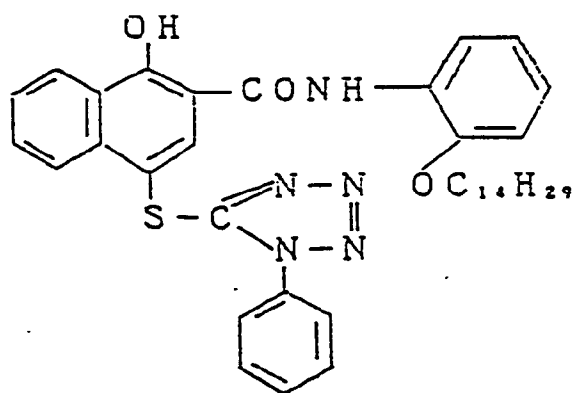
Cyan Coupler (C-7):



Emulsion (2)

(i)	10 wt% Gelatin Aqueous Solution	1,000 g
(ii)	Sodium p-Dodecylbenzenesulfonate	5 g
	Tricresyl Phosphate	60 cm ³
	Cyan Coupler (C-7)	6 g
	DIR Cyan Coupler*	64 g
	Ethyl Acetate	100 cm ³

* DIR Cyan Coupler:



Second Layer: Red-Sensitive Silver Halide Middle Sensitive Layer

(1-b) Preparation of an Emulsion Solution for Forming Middle-Sensitive Emulsion Layer

The following changes were conducted in the above-described (1-a).

Average grain size of emulsion: 0.9 μ m

Amount of added red-sensitive sensitizing agent: 140 cm³

Amount of added emulsion: Emulsion (1), 240 g Emulsion (2), 10 g

Third Layer: Red-Sensitive Silver Halide High Sensitive Layer

(1-c) Preparation of an Emulsion Solution for Forming High Sensitive Emulsion Layer

The following changes were conducted in the above (1-a).

Average grain size of emulsion: 1.1 μ m (grains of 1.0 μ m or more in size accounting for 50 wt% of the total grains)

Amount of added red-sensitive sensitizing agent: 100 cm³

Amount of added emulsion: Emulsion (1), 150 g

Fourth Layer: Gelatin Interlayer

Fifth Layer: Green-Sensitive Silver Halide Low Sensitive Layer

(2-a) Preparation of an Emulsion Solution for Forming Low Sensitive Emulsion

A silver bromoiodide emulsion containing 6 mol% iodide (average grain size: 0.6 μ m; containing 100 g of silver halide and 70 g of gelatin per kg of emulsion) was prepared in a conventional manner. To 1 kg of this emulsion were added 200 cm³ of a 0.1 wt% methanol solution of 3,3'-di(3-sulfoethyl)-9-ethylbenzoxacarbocyanine pyridinium salt as a green-sensitive sensitizing agent. Then, 20 cm³ of a 5 wt% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine were added thereto, and 380 g of Magenta Coupler Emulsion (3) and 20 g of Magenta Coupler Emulsion (4) of the following formulations were added thereto.

Further, 50 cm³ of a 2 wt% aqueous solution of 2-hydroxy-4,6-dichlorotriazine sodium salt were added thereto as a gelatin hardener to prepare an emulsion solution for forming a low sensitive emulsion.

Emulsion (3)

	(i)	10 wt% Gelatin Aqueous Solution	1,000 g
	(ii)	Sodium p-Dodecylbenzenesulfonate	5 g
5		Tricresyl Phosphate	65 cm ³
		Magenta Coupler (M-7)	6 g
10		Ethyl Acetate	110 cm ³

A mixture of (ii) was made into a solution at 55°C, and the resulting solution was added to (i) previously heated to 55°C, followed by emulsification in a colloid mill.

Magenta Coupler (M-7):

15 1-(2,4,6-trichlorophenyl)-3-[3-(2,4-di-t-pentylphenoxyacetamido)benzamido]-5-pyrazolone
Emulsion (4)

20

25

30

35

40

45

50

55

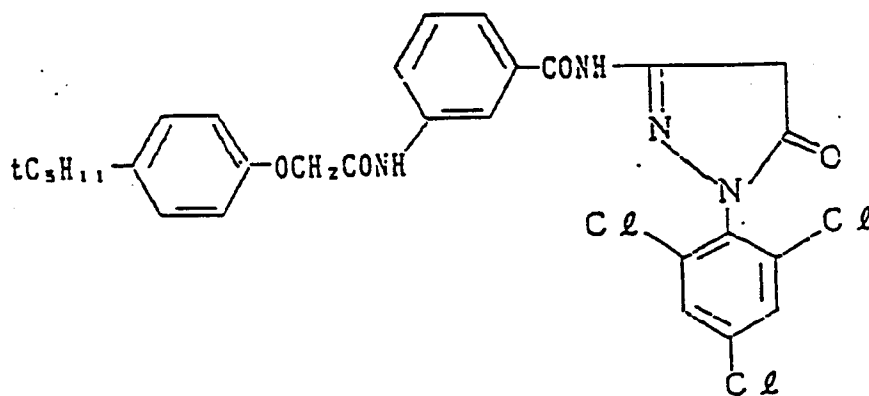
(i)	10 wt% Gelatin Aqueous Solution	1,000 g
(ii)	Sodium p-Dodecylbenzenesulfonate	5 g
	Tricresyl Phosphate	65 cm ³
	Magenta Coupler*	63 g
	DIR Magenta Coupler**	60 g
	Ethyl Acetate	110 cm ³

Emulsification was conducted in the same manner as with Emulsion (3).

** DIR Magenta Coupler:

1-{4-[2-(2,4-di-t-pentylphenoxy)butanamido]phenyl}-3-(1-pyrrolidinyl)-4-(1-phenyltetrazolyl-5-thio)-5-pyrazolone

* Magenta Coupler:



Sixth Layer: Green-Sensitive Silver Halide Middle Sensitive Layer

(2-b) Preparation of an Emulsion Solution for Forming Middle-Sensitive Emulsion Layer

A silver bromiodide emulsion containing 5 mol% of iodide (average grain size: 0.9 μ m; containing 100 g of silver halide and 70 g of gelatin per kg of emulsion) was prepared in a conventional manner. To 1 kg of this emulsion were added 150 cm³ of a methanol solution of the green-sensitive sensitizer shown in (2-a). Then, 20 cm³ of a 5 wt% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine were added thereto. Further, 285 g of the above-described Emulsion (3) and 15 g of the above-described Emulsion (4) were added thereto.

In addition, 50 cm³ of a 2 wt% aqueous solution of 2-hydroxy-4,6-dichlorotriazine sodium salt were added thereto as a gelatin hardener to prepare an emulsion solution for forming a middle sensitive emulsion.

Seventh Layer: Green-Sensitive Silver Halide High Sensitive Layer

(2-c) Preparation of an Emulsion Solution for Forming High Sensitive Emulsion Layer

A silver bromiodide emulsion containing 6 mol% iodide (average grain size: 1.1 μ m; 50 wt% of the grains based on the whole grains having a grain size of 1.0 μ m or more; containing 100 g of silver halide

and 70 g of gelatin per kg of emulsion) was prepared in a conventional manner. To 1 kg of this emulsion were added 80 cm³ of a methanol solution of the green-sensitive sensitizing agent shown in (2-a). Then, 20 cm³ of a 5 wt% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine were added thereto and, further, 200 g of Emulsion (3) were added thereto.

50 cm³ of a 2 wt% aqueous solution of 2-hydroxy-4,6-dichlorotriazine sodium salt were further added thereto as a gelatin hardener to prepare an emulsion solution for forming a high sensitive emulsion.

Eighth Layer: Yellow Filter Layer (dry thickness: 1.2 μm) Comprising Yellow Colloidal Silver

Ninth Layer: Blue-Sensitive Silver Halide Low Sensitive Layer

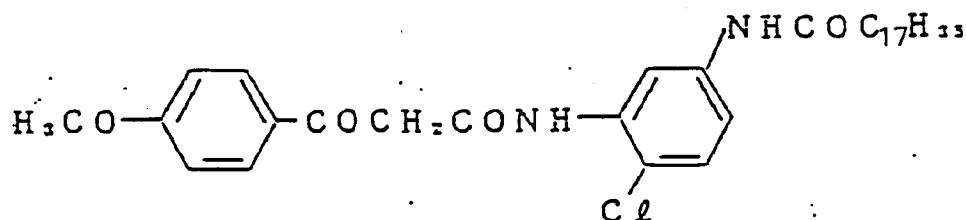
(3-a) Preparation of an Emulsion Solution for Forming Low Sensitive Emulsion Layer

A silver bromoiodide emulsion containing 5 mol% iodide (average grain size: 0.6 μm; containing 100 g of silver halide and 70 g of gelatin per kg of the emulsion) was prepared in a conventional manner. To 1 kg of this emulsion were added 20 cm³ of a 5 wt% aqueous solution of 5-methyl-7-hydroxy-2,3,4-triazaindolizine and 600 g of Yellow Coupler Emulsion (5) of the following formulation. Further, 50 cm³ of a 2 wt% aqueous solution of 2-hydroxy-4,6-dichlorotriazine sodium salt were added thereto as a gelatin hardener to prepare an emulsion solution for forming a low sensitive emulsion.

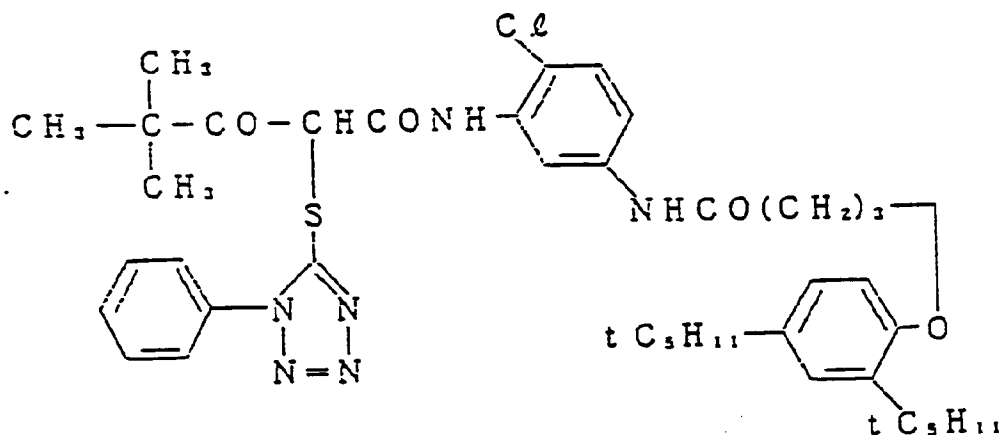
Emulsion (5)

(i)	10 wt% Gelatin Aqueous Solution	1,000 g
(ii)	Sodium p-Dodecylbenzenesulfonate	5 g
	Tricresyl Phosphate	80 cm ³
	Yellow Coupler*	100 g
	Yellow DIR Coupler**	10 g
	Ethyl Acetate	120 cm ³

* Yellow Coupler:



** Yellow DIR Coupler



Tenth Layer: Blue-Sensitive Silver Halide Middle Sensitive Layer

The following changes were conducted in the above (3-a).

Average grain size of emulsion: 0.9 μm

Amount of added emulsion: 400 g

Eleventh Layer: Blue-Sensitive Silver Halide High Sensitive Layer

The following changes were conducted in the above (3-a).

Average grain size of emulsion: 1.1 μm (provided that grains larger than 1.0 μm account for 50 wt% of the total grains)

Amount of added emulsion: 200 g

Twelfth Layer: Surface Protecting Layer

10 wt% Gelatin Solution	1,000 cm^3
Sodium Dodecylbenzenesulfonate	40 mg
SiO_2 Fine Particles (3.0 μm)	50 mg
Sodium Polystyrenesulfonate	1 g
2-Hydroxy-4,6-dichlorotriazine	50 mg

Additionally, amounts of coated silver for the respective light-sensitive layers described above were as follows: first layer (1.0 g/m^2); second layer (0.8 g/m^2); third layer (1.2 g/m^2); fifth layer (1.2 g/m^2); sixth layer (1.0 g/m^2); seventh layer (1.2 g/m^2); ninth layer (0.6 g/m^2); tenth layer (0.6 g/m^2); and eleventh layer (0.6 g/m^2).

The thus-obtained color negative film was cut into a 35 mm size, and was loaded in a cartridge. After leaving it for 10 days at 40°C, photographing was conducted using an ordinary camera, followed by development processing the film as follows.

<u>Processing Step</u>	<u>Temperature</u> (°C)	<u>Time</u> (min)
Color Development	38	3
Stopping	"	1
Washing with Water	"	1
Bleaching	"	2
Washing with Water	"	1
Fixing	"	2
Washing with Water	"	1
Stabilizing Bath	"	1

Processing solutions used have the following formulations.

Color Developer:

5	Sodium Hydroxide	2 g
	Sodium Sulfite	2 g
	Potassium Bromide	0.4 g
10	Sodium Chloride	1 g
	Borax	4 g
	Hydroxylamine Sulfate	2 g
15	Disodium Ethylenediaminetetraacetate Dihydrate	2 g
	4-Amino-3-methyl-N-ethyl-N-(β -hydroxyethyl)aniline Monosulfate	4 g
20	Water to make	1 l

Stopping Bath:

25	Sodium Thiosulfate	10 g
	Ammonium Thiosulfate (70 wt% aq. soln.)	30 ml
30	Acetic Acid	30 ml
	Sodium Acetate	5 g
35	Potash Alum	15 g
	Water to make	1 l

Bleaching Solution:

40	Iron(III) Sodium Ethylenediaminetetraacetate Dihydrate	100 g
	Potassium Bromide	50 g
45	Ammonium Nitrate	50 g
	Borax	5 g
50	Aqueous Ammonia to adjust pH to 5.0	
	Water to make	1 l

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Fixing Solution:

5	Sodium Thiosulfate	150 g
	Sodium Sulfite	15 g
	Borax	12 g
10	Glacial Acetic Acid	15 ml
	Potash Alum	20 g
	Water to make	1 l

Stabilizing Bath:

20	Borax	5 g
	Sodium Citrate	5 g
	Sodium Metaborate (tetrahydrate)	3 g
25	Potash Alum	15 g
	Water to make	1 l

30 The curling state after development processing was as follows. Light-sensitive materials containing a commercially available PET film as a support failed to extinguish curling properties, whereas light-sensitive materials containing polyester film of the present invention scarcely curled.

The light-sensitive material of the present invention contains as a support a polyester film with an excellent mechanical strength, and enables removal of curling properties while maintaining the mechanical properties.

35 COMPARATIVE EXAMPLE 1

A 50 μ m thick biaxially stretched polyester film having an intrinsic viscosity of 0.67 was prepared in the same manner as described in Example 1 except that 10 parts by weight of polyethylene glycol having a molecular weight of 4,000 were used in place of the same amount of dimethyl adipate. The resulting film had a haze of 4.5%, a breaking strength of 8 kg/mm², an initial modulus of 320 kg/mm², and very poor transparency. When this film was not subjected to a heat treatment for the measurement of haze, it had a high transparency and had a haze of 2.0%.

45 A light-sensitive material was prepared in the same manner as described in Example 1 using the biaxially stretched polyester film obtained above. After development treatment, the exposed part of the film became opaque and developed images were not sharp. It is clear from the above that the polyester film prepared in Comparative Example 1 above is not useful as a support for a light-sensitive material.

50 Since the light-sensitive materials of the present invention have excellent mechanical properties and enable easy extinguishing of curling, they permit a marked reduction in the thickness of the support even when used as roll films and therefore render the size of the cartridge compact or, in using the same cartridge, enable loading of longer film. The polyester film of the present invention can be produced at a low casting temperature and is not broken upon stretching and, in spite of its high water content, it maintains the essential merits of polyester film.

In addition, it suffers extremely less precipitation of oligomers in spite of the high water content, thus suffering no detrimental influences on photographic properties.

55 Further, it enables reduction of the humidity of the wrapping case of light-sensitive materials, and hence photographic properties change less with time.

Claims

1. A photographic light-sensitive material, which comprises a polyester film support having provided thereon at least one light-sensitive silver halide emulsion layer, said polyester film having a haze of up to 3%, a water content of from 0.5 wt.-% to 5.0 wt.-%, a curl-extinguishing ratio of 50% or more, and containing as predominant constituents terephthalic acid component and a glycol component, said polyester film further comprising an aliphatic dicarboxylic acid component having 4 to 20 carbon atoms as a copolymerization component in an amount of from 3 to 25 mol% based on the terephthalic acid component, wherein the haze is measured in accordance with ASTM D1003-52 after heat treatment of the film at a temperature of 150°C for ten minutes, the water content is measured after first moisture-conditioning the film under conditions of 23°C and 30% RH for three hours, next dipping the film in distilled water at 23°C for fifteen minutes and then measuring the water content using a micro-moisture meter at a drying temperature of 150°C, and the curl-extinguishing ratio is measured after first dipping the film in distilled water at 40°C for fifteen minutes, and then drying for three minutes in air in a thermostatic chamber maintained at 55°C while applying a load of 50g.
2. The photographic light-sensitive material as claimed in claim 1, wherein said polyester film is a polyester film containing an aromatic dicarboxylic acid having a metal sulfonate group as a copolymerization component and having a breaking strength of from 8 to 25 kg/mm² and an initial modulus of from 200 to 500 kg/mm².
3. The photographic light-sensitive material as claimed in claims 1 or 2, wherein said polyester film is a copolymerized polyethylene terephthalate film.
4. The photographic light-sensitive material as claimed in claim 2, wherein said aromatic dicarboxylic acid having a metal sulfonate group is selected from the group consisting of 5-sodium sulfoisophthalic acid, 5-potassium sulfoisophthalic acid, 5-lithium sulfoisophthalic acid, 2-sodium sulfoterephthalic acid, 2-potassium sulfoterephthalic acid, 2-lithium sulfoterephthalic acid, 4-sodium sulfophthalic acid, 4-potassium sulfophthalic acid, 4-lithium sulfophthalic acid, 4-sodium sulfo-2,6-naphthalenedicarboxylic acid, 4-potassium sulfo-2,6-naphthalenedicarboxylic acid, and 4-lithium sulfo-2,6-naphthalenedicarboxylic acid.
5. The photographic light-sensitive material as claimed in claim 2, wherein said polyester film mainly comprises terephthalic acid as a dicarboxylic acid component, and the copolymerization amount of said aromatic dicarboxylic acid component having a metal sulfonate group is 2 to 15 mol% based on the terephthalic acid component.
6. The photographic light-sensitive material as claimed in claim 1, wherein said aliphatic dicarboxylic acid component is selected from the group consisting of succinic acid, adipic acid and sebacic acid.
7. The photographic light-sensitive material as claimed in claim 1, wherein a polyalkylene glycol is used as an additional copolymerizable component.
8. The photographic light-sensitive material as claimed in claim 3, wherein said polyester film contains a dye.
9. The photographic light-sensitive material as claimed in claim 3, wherein said polyester film has a subbing layer on its surface.
10. The photographic light-sensitive material as claimed in claim 1, wherein said light-sensitive material is a roll film.
11. The photographic light-sensitive material as claimed in claim 1, wherein said polyester film has a curl-extinguishing ratio of 80% or more.
12. The photographic light-sensitive material as claimed in claims 1 or 2, wherein said polyester film has a thickness of from 25 to 250 µm.
13. The photographic light-sensitive material as claimed in claim 12, wherein said polyester film has a thickness of from 40 to 150 µm.

Patentansprüche

1. Photographisches lichtempfindliches Material, umfassend einen Polyesterfilmträger mit wenigstens einer
 5 darauf angeordneten lichtempfindlichen Silberhalogenidemulsionsschicht, wobei der Polyesterfilm einen
 Schleier von bis zu 3%, einen Wassergehalt von 0,5 Gew.-% bis 5,0 Gew.-%, ein Kräusel-Löschverhältnis
 von 50% oder mehr besitzt und als vorherrschende Bestandteile eine Terephthalsäurekomponente und
 eine Glykolkomponente besitzt, wobei der Polyesterfilm weiterhin eine aliphatische Dicarbonsäurekom-
 10 ponente mit 4 bis 20 Kohlenstoffatomen als Copolymerisationskomponente in einer Menge von 3 bis 25
 Mol%, bezogen auf die Terephthalsäurekomponente, besitzt, worin der Schleier im Einklang mit ASTM
 D1003-52 nach einer Wärmebehandlung des Films bei einer Temperatur von 150°C für 10 Minuten ge-
 messen wird, und der Wassergehalt gemessen wird, nachdem zuerst der Film unter den Bedingungen
 15 von 23°C und 30% RH für 3 Stunden auf Feuchtigkeit eingestellt worden ist, und als nächstes der Film
 in destilliertes Wasser bei 23°C für 15 Minuten eingetaucht wird und anschließend der Wassergehalt unter
 Verwendung einer Mikrofeuchtigkeitsmeßvorrichtung bei einer Trocknungstemperatur von 150°C gemes-
 sen wird, und das Kräusel-Löschverhältnis gemessen wird, nachdem zuerst der Film in destilliertes Was-
 ser bei 40°C für 15 Minuten eingetaucht worden ist und anschließend für 3 Minuten in Luft in einer bei
 55°C gehaltenen thermostatischen Kammer unter Anwendung einer Belastung von 50 g getrocknet wor-
 den ist.
2. Photographisches lichtempfindliches Material nach Anspruch 1, worin der Polyesterfilm ein Polyesterfilm
 20 ist, enthaltend eine aromatische Dicarbonsäure mit einer Metallsulfonatgruppe als eine Copolymerisati-
 onskomponente und eine Bruchfestigkeit von 8 bis 25 kg/mm² und einem anfänglichen Modul von 200
 bis 500 kg/mm² besitzt.
3. Photographisches lichtempfindliches Material nach Anspruch 1 oder 2, worin der Polyesterfilm ein copo-
 25 lymerisierter Polyethylenterephthalatfilm ist.
4. Photographisches lichtempfindliches Material nach Anspruch 2, worin die aromatische Dicarbonsäure mit
 30 einer Metallsulfonatgruppe ausgewählt ist aus der Gruppe, bestehend aus 5-Natriumsulfoisophthalsäure,
 5-Kaliumsulfoisophthalsäure, 5-Lithiumsulfoisophthalsäure, 2-Natriumsulfoterephthalsäure, 2-Kalium-
 sulfoterephthalsäure, 2-Lithiumsulfoterephthalsäure, 4-Natriumsulfophthalsäure, 4-Kaliumsulfophthal-
 säure, 4-Lithiumsulfophthalsäure, 4-natriumsulfo-2,6-naphthalindicarbonsäure, 4-Kaliumsulfo-2,6-
 naphthalindicarbonsäure und 4-Lithiumsulfo-2,6-naphthalindicarbonsäure.
5. Photographisches lichtempfindliches Material nach Anspruch 2, worin der Polyesterfilm hauptsächlich Te-
 35 rephthalsäure als Dicarbonsäurekomponente umfaßt, und die Copolymerisationsmenge der aromati-
 schen Dicarbonsäurekomponente mit einer Metallsulfonatgruppe 2 bis 15 Mol%, bezogen auf die Tereph-
 thalsäurekomponente, beträgt.
6. Photographisches lichtempfindliches Material nach Anspruch 1, worin die aliphatische Dicarbonsäure-
 40 komponente ausgewählt ist aus der Gruppe, bestehend aus Succinsäure, Adipinsäure und Sebacinsäure.
7. Photographisches lichtempfindliches Material nach Anspruch 1, worin ein Polyalkylenglykol als eine zu-
 sätzliche copolymerisierbare Komponente verwendet wird.
8. Photographisches lichtempfindliches Material nach Anspruch 3, worin der Polyesterfilm einen Farbstoff
 45 enthält.
9. Photographisches lichtempfindliches Material nach Anspruch 3, worin der Polyesterfilm eine Unterschicht
 auf seiner Oberfläche trägt.
10. Photographisches lichtempfindliches Material nach Anspruch 1, worin das lichtempfindliche Material ein
 50 Rollenfilm ist.
11. Photographisches lichtempfindliches Material nach Anspruch 1, worin der Polyesterfilm ein Kräusel-
 Löschverhältnis von 80% oder mehr besitzt.
12. Photographisches lichtempfindliches Material nach Anspruch 1 oder 2, worin der Polyesterfilm eine Dicke
 55 von 25 bis 250 µm besitzt.

13. Photographisches lichtempfindliches Material nach Anspruch 12, worin der Polyesterfilm eine Dicke von 40 bis 150 μm besitzt.

5 Revendications

1. Matériau photographique photosensible, qui comporte un support en film polyester portant au moins une couche d'émulsion photosensible à l'halogénure d'argent, ledit film polyester présentant un voile d'au plus 3%, une teneur en eau de 0,5% en poids à 5,0% en poids, un taux de disparition de la courbure de 50% ou davantage, et contenant comme constituants principaux un composant acide téréphtalique et un composant glycol, ledit film polyester 10 comportant en outre un composant acide dicarboxylique aliphatique présentant de 4 à 20 atomes de carbone, comme composant de copolymérisation, en quantité de 3 à 25 mole % calculés sur le composant acide téréphtalique, dans lequel le voile est mesuré conformément à ASTM D1003-52 15 après traitement thermique du film à une température de 150°C pendant dix minutes, la teneur en eau est mesurée après un premier conditionnement à l'humidité du film dans les conditions de 23°C et 30% d'humidité relative pendant trois heures, et en plongeant ensuite le film dans l'eau 20 distillée à 23°C pendant quinze minutes, et en mesurant alors la teneur en eau à l'aide d'un micro-hygromètre, à une température de séchage de 150°C, et le taux de disparition de la courbure est mesuré après avoir d'abord plongé le film dans l'eau distillée à 40°C pendant quinze 25 minutes, et en le séchant alors à l'air pendant trois minutes, dans une chambre thermostatée maintenue à 55°C, tout en appliquant une charge de 50 g.
2. Matériau photographique photosensible selon la revendication 1, dans lequel ledit film polyester est un 30 film polyester contenant un acide dicarboxylique aromatique présentant un radical sulfonate de métal comme composant de copolymérisation, et présentant une résistance à la rupture de 8 à 25 kg/mm² et un module initial de 200 à 500 kg/mm².
3. Matériau photographique photosensible selon la 35 revendication 1 ou 2, dans lequel ledit film polyester est un film de téréphtalate de polyéthylène copolymérisé.
4. Matériau photographique photosensible selon la revendication 2, dans lequel ledit acide dicarboxylique aromatique présentant un radical sulfonate de métal est choisi dans le groupe constitué de l'acide 5-sodium sulfoisophtalique, l'acide 5-potassium sulfoisophtalique, l'acide 5-lithium sulfoisophtalique, l'acide 2-sodium sulfotéréphtalique, l'acide 2-potassium sulfotéréphtalique, l'acide 2-lithium sulfotéréphtalique, l'acide 4-sodium sulfophtalique, l'acide 4-potassium sulfophtalique, l'acide 4-lithium sulfophtalique, l'acide 4-sodium sulfo-2,6-naphtalènedicarboxylique, l'acide 4-potassium sulfo-2,6-naphtalènedicarboxylique et l'acide 4-lithium sulfo-2,6-naphtalènedicarboxylique.
5. Matériau photographique photosensible selon la revendication 2, dans lequel ledit film polyester comporte principalement de l'acide téréphtalique comme composant acide dicarboxylique, et le taux de copolymérisation dudit composant acide dicarboxylique aromatique présentant un radical sulfonate de métal est de 2 à 15 mole %, calculé sur le composant acide téréphtalique.
6. Matériau photographique photosensible selon la revendication 1, dans lequel ledit composant acide dicarboxylique aliphatique est choisi dans le groupe constitué de l'acide succinique, de l'acide adipique et de l'acide sébacique.
7. Matériau photographique photosensible selon la revendication 1, dans lequel on utilise comme composant copolymérisable supplémentaire un polyalkylèneglycol.
8. Matériau photographique photosensible selon la revendication 3, dans lequel ledit film polyester contient un colorant.
9. Matériau photographique photosensible selon la revendication 3, dans lequel ledit film polyester présente à sa surface une couche de fond.
10. Matériau photographique photosensible selon la revendication 1, dans lequel ledit matériau photosensible est un film en rouleau.

- 11.** Matériau photographique photosensible selon la revendication 1, dans lequel ledit film polyester présente un taux de disparition de la courbure de 80% ou davantage.
- 12.** Matériau photographique photosensible selon les revendications 1 ou 2, dans lequel ledit film polyester présente une épaisseur de 25 à 250 μm .
- 13.** Matériau photographique photosensible selon la revendication 12, dans lequel ledit film polyester présente une épaisseur de 40 à 150 μm .

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