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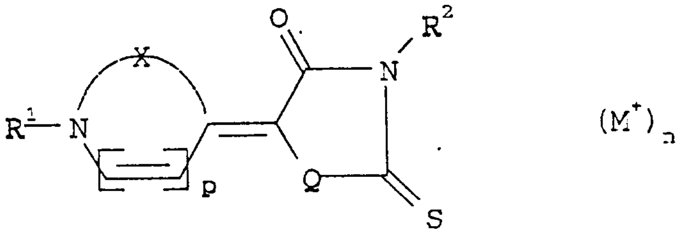
(54) Method to spectrally sensitize tabular silver halide grains

(57) A method is disclosed for manufacturing a tabular silver halide emulsion wherein the tabular silver halide grains have an aspect ratio of at least 2:1, an average crystal diameter between 0.3 µm and 3.0 µm and an average thickness of less than 0.50 µm, and more preferably less than 0.3 µm, for at least 50 % of the total projective surface area of said grains, and wherein said method comprises the steps of precipitating said grains, spectrally sensitizing and chemically ripening, characterized by adding to the emulsion before and/or during chemically ripening at least one spectrally sensitizing dye corresponding to the general formula (I)



(I)

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Description

FIELD OF THE INVENTION.

The present invention relates to spectrally sensitized silver halide emulsions comprising tabular crystals, to the preparation method thereof and to light-sensitive photographic materials containing said emulsions.

BACKGROUND OF THE INVENTION

The effects of various precipitation conditions on the formation of silver halide emulsions comprising tabular crystals have been studied extensively as the said tabular grains are known in the photographic art for quite some time. As early as 1961 Berry et al. described the preparation and growth of tabular silver bromoiodide grains in Photographic Science and Engineering, Vol 5, No 6. A discussion of tabular grains appeared in Duffin, Photographic Emulsion Chemistry, Focal Press, 1966, p. 66-72. Early patent literature includes US-P's 4,063,951; 4,067,739; US-P 4,150,994; 4,184,877 and 4,184,878. However the tabular grains described herein cannot be regarded as showing a high diameter to thickness ratio, commonly termed aspect ratio. In a number of US applications filed in 1981 and issued in 1984 tabular grains with high aspect ratio and their advantages in photographic applications are described as, e.g., in US-P's 4,434,226; 4,439,520; 4,425,425; 4,425,426 and 4,433,048. A survey on high aspect ratio silver halide emulsions appeared in Research Disclosure, Vol 225, Jan 1983, Item 22534.

The above cited references on tabular grains are mainly concerned with high sensitive silver bromide or silver iodobromide emulsions.

Tabular grain emulsions having a high aspect ratio are known to provide several advantages over more conventional spherical grains as, e.g., a high covering power, a high (spectral) sensitivity and a lower coating weight, which saves costs in manufacturing. Said lower coating weight is especially preferred if rapid processing applications are required, which is nowadays an ever more returning demand.

Spectrally sensitizing dyes are well known in the art of photography for green and red sensitization of flat tabular grains, but for blue and/or ultraviolet sensitization the number of examples is rather limited. Recently arylidene sensitizing dyes for tabular grains have been disclosed in WO 93/11458. Spectral supersensitization of tabular silver halide grains with J-aggregate forming benzothiazolorhodanine zeromethine-merocyanines in combination with a tetraazaindene derivative has been described in EP-A 00 487 010. One particular sensitizer which is frequently mentioned in the patent literature is 3-ethyl-5-[1-(4-sulfobutyl)-4-(1H)-pyridylidene] rhodanine, as, e.g., in EP-A 0 300 382; in EP-A 0 404 142; in EP-A 0 438 135 and in EP-A 0 509 519.

Further it is known to use in radiography combinations of green-emitting phosphor screens with film materials containing spectrally sensitized tabular grain emulsions. From the viewpoint of sharpness new combinations of blue and ultra-violet emitting radiographic screens with silver halide elements comprising tabular grains with an increased sensitivity in the same region of the electromagnetic spectrum would be highly appreciated.

The provision of blue sensitizing dyes for spectrally sensitizing tabular grains in addition to their inherent sensitivity to blue light in order to get improved image quality (sharpness) poses problems, especially related to (yellow) dye stain after processing materials.

OBJECTS OF THE INVENTION

Therefor it is an object of the present invention to provide emulsions comprising spectrally sensitized silver halide tabular grains showing an improvement in sensitivity (speed) to blue and ultra-violet radiation and a method to prepare said emulsions.

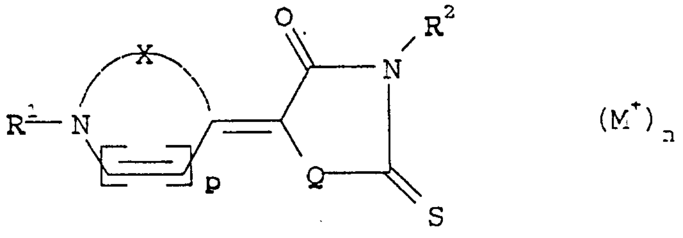
It is another object to provide radiographic screen-film combinations comprising at least one X-ray intensifying screen in operative association with a photographic element comprising tabular grains spectrally sensitized to the blue and ultra-violet spectral region.

Moreover it is an object to provide photographic elements which for being subjected after exposure to rapid processing, show high sensitivity, high image quality and good physical properties, especially no dye stain and brilliant surface characteristics.

Other objects will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

According to this invention a method is provided for manufacturing a tabular silver halide emulsion wherein the tabular silver halide grains have an aspect ratio of at least 2:1, an average crystal diameter between 0.3 µm and 3.0 µm and an average thickness of less than 0.50 µm, and more preferably less than 0.3 µm, accounting for at least 50 % of the total projective surface area of said grains, and wherein said method comprises the steps of precipitating said grains, spectrally sensitizing and chemically ripening, characterized by adding to the emulsion before and/or during chemically ripening at least one spectrally sensitizing dye corresponding to the general formula (I)



(I)

wherein
X represent the atoms, necessary to form a heterocyclic 5- or 6-membered ring (as is typical for cyanine dyes);
Q represents S, NR^3, O, or $-(C=O)-N(R^4)-$;
M^+ represents a kation, e.g., Li^+, Na^+, K^+, $HN^+(C_2H_5)_3$;
n equals 0, 1, or 2;
p equals 0 or 1;
R^1, R^2, R^3 and R^4 each independently represent a substituted or unsubstituted C_1-C_5 alkyl chain, with the proviso that at least one of R^2, R^3 and R^4 has a solubilizing group as, e.g.,
$(CH_2)_mSO_3^-$ or $(CH_2)_mN(R)SO_3^-$ wherein m equals 1, 2, 3 or 4, wherein R has the same meaning as R^1 to R^4;
$(CH_2)_2CH(Y)SO_3^-$ wherein Y represents CH_3-, -Cl or -OH;
$(CH_2)_qOSO_3^-$ wherein q equals 2 or 3;
$(CH_2)_rCO_2^-(H^+)$ wherein r equals 1, 2 or 3;
$(CH_2)_sSO_2^-(CH_2)_tH$ wherein s equals 2 or 3 and t equals 1 or 2;
$(CH_2)_x$-Phen-W, wherein W represents $-COO^-$ or SO_3^-; Phen represents phenyl which is substituted or unsubstituted; and x equals 1, 2, 3 or 4;
or a latent solubilizing group as, e.g.,
$(CH_2)_{m'}-(C=O)-O-CH_2-(C=O)-CH_3$, wherein m' is an integer having a value of from 1 to 5.

Moreover according to this invention a light-sensitive silver halide emulsion is provided, comprising tabular grains spectrally sensitized by the method disclosed hereinbefore, as well as a photographic material comprising a support and on at least one side of said support at least one hydrophilic colloid layer and at least one photosensitive layer comprising at least one photographic silver halide emulsion with tabular grains spectrally sensitized as defined and wherein the total amount of silver coated on one side of said support, expressed as the equivalent amount of silver nitrate, is less than 10 g/m^2, more preferably less than 7 g/m^2, and still more preferably less than 5.5 g/m^2 and wherein the time to dissolve the coated layers of said material, determined by the method disclosed herein, is not less than 45 minutes.

A radiographic element comprising at least one ultra-violet and blue light emitting X-ray intensifying screen in operative association with said photographic material is also provided.

DETAILED DESCRIPTION.

Silver halide tabular grains used in the method of this invention are crystals possessing two parallel faces with a ratio between the diameter of a circle having the same area as these faces, and the thickness, being the distance between the two major faces, equal to at least 2:1.

For radiographic applications the main photographic advantages of tabular grains compared to normal globular grains are a high covering power at high forehardening levels, a high developability and a higher sharpness especially in double side coated spectrally sensitized materials.

The light-sensitive silver halide emulsions comprising tabular grains used in the method according to this invention, are characterized by an average grain thickness of not more than 0.5 µm, and more preferably not more than 0.3 µm, with an average aspect ratio of at least 2:1, and more preferably at least 5:1. For practical use, an aspect ratio between 5:1 and 8:1 is recommended.

As thinner tabular grains provide the advantages mentioned hereinbefore to a larger extent, more preferred grains used according to this invention have an average grain thickness of not more than 0.2 µm and not less than 0.05 µm.

From electron microscopic photographs taken from the silver halide tabular crystals, it is possible to calculate the average grain thickness and the average crystal diameter of a circle, having a surface equivalent with the crystal surface.

Moreover in a preferred embodiment the light-sensitive tabular silver halide grains used in the method according to this invention account for a total projective area of at least 70% and a total projective area of at least 90% is even more preferred.

Emulsions comprising tabular silver halide grains in accordance with this invention preferably have silver halide compositions as, e.g., silver chloride, silver chlorobromide, silver chlorobromoiodide, silver chloroiodide, silver bromide or silver bromoiodide. Iodide ions can be provided in the preparation step by anorganic iodide salts and/or organic compounds releasing iodide ions as has e.g. been described in EP-A's 0 561 415, 0 563 701 and 0 563 708, and in EP-A's 0 649 052 and 0 651 284, which are incorporated herein by reference. Iodide ion concentrations up to 10 mole % may be present but concentrations up to 3 mole % are particularly preferred.

The preparation in gelatinous medium used as a protective colloid of light-sensitive tabular silver bromide and silver bromoiodide emulsions has been described in EP-A 0 569 075, which application is incorporated herein by reference. Further the preparation of light-sensitive tabular emulsions rich in chloride has been described, e.g., in EP-A 0 481 133, which is incorporated herein by reference as well.

Silica sols can be used as a protective colloid instead of gelatin for the preparation of tabular silver bromide and silver bromoiodide emulsions that are spectrally sensitized according to this invention as has been described in EP-A No. 94200932, filed April 6, 1994 and in EP-A No. 94200933, wherein the preparation of tabular grains rich in chloride has been described. Both Applications are incorporated herein by reference.

The photographic emulsions according to this invention, comprising silver halide tabular crystals may have a homogeneous or a heterogeneous halide distribution within the crystal volume. A heterogeneous halide distribution may be obtained by application of growth steps having a different halide composition or by conversion steps, e.g., by addition of halide ions that provide less soluble silver salts, onto existing tabular cores. In the case of a heterogenous distribution of halide ions a multilayered grain structure is obtained. Obviously the tabular form has to be maintained in this case, in order to get tabular emulsion crystals in accordance with this invention.

The crystals may further be doped with whatever a dope, as e.g. with Rh^{3+}, Ir^{4+}, Cd^{2+}, Zn^{2+}, Pb^{2+}.

During precipitation grain growth restrainers or accelerators may be added to obtain crystals with a preferred average crystal size between 0.05 and 5 μm. Examples of grain growth accelerators are compounds carrying, e.g., a thioether function as methionine or 1,8-dihydroxy-3,6,-dithiooctane.

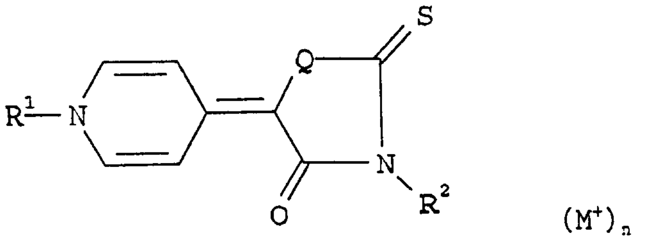
It is important to avoid renucleation during the growth step of the nuclei formed in the nucleation step by controlling the preferred increasing rate of addition of the silver nitrate and the halide salts to make the distribution predictable of the emulsion crystals.

Silver halide nuclei can also be formed in a separate vessel and added to the reaction vessel wherein the growth step is performed.

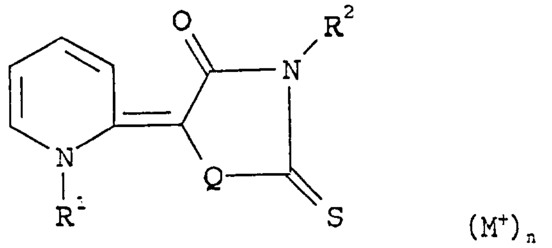
The light-sensitive emulsion comprising silver halide tabular crystals, prepared in accordance with the present invention is, after redispersion, a so-called primitive emulsion. However, said emulsion can be chemically sensitized as described i.a. "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in this literature chemical sensitization can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur, selenium and/or tellurium, e.g., thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodanines or the corresponding selenium or tellurium compounds thereof. The emulsions can be sensitized also by means of gold-sulphur, gold-selenium or gold-tellurium ripeners or by means of reductors, e.g., tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Combinations of sulphur, selenium and gold ion providing compounds in the chemical ripening step of blue sensitized tabular grain emulsions prepared according to the method of this invention are particularly preferred as an improved sensitivity is obtained for an equal or even lower fog level than the one obtained with the classical sulphur and gold providing ripening agents and as preservation characteristics of the material in which said emulsions are used are remarkably improved. Moreover tabular grain emulsions according to this invention are less sensitive to darkroom light. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used. A mixture can also be made of two or more separately precipitated emulsions being chemically sensitized before mixing them.

According to this invention spectral sensitization is performed before and/or during chemical ripening, with at least one blue and/or ultra violet light absorbing spectral sensitiser according to the formula (I), given above. In classical emulsion preparation spectral sensitization traditionally follows the completion of chemical sensitization. However, in connection with tabular grains, and especially with the tabular grains used in the method according to this invention it is specifically contemplated that spectral sensitization occurs simultaneously with or even precedes completely the chemical sensitization step; the chemical sensitization after spectral sensitization is believed to occur at one or more ordered discrete sites of tabular grains. With the emulsions of the present invention, the chemical sensitization may further proceed in the presence of one or more 1-phenyl-3-pyrazolidine-1-one compound and derivatives, dihydroxy benzene, e.g., hydroquinone, resorcinol, catechol and/or derivative(s) thereof, one or more stabilizer(s) or antifoggant(s), one or more spectral sensitizer(s) or combinations of said ingredients.

In a preferred embodiment according to this invention tabular silver halide emulsion crystals are spectrally sensitized with at least one dye having a structure corresponding to the formula (II) or (III) given below.



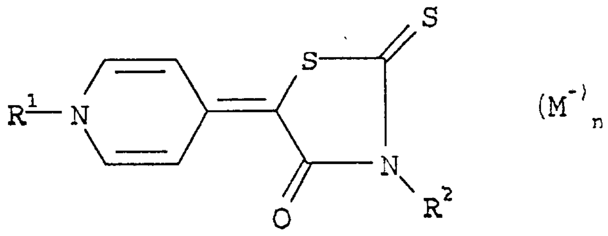
(II)



(III)

wherein all symbols have the same meaning as in formula (I) given hereinbefore.

More preferred structures of the blue sensitizing dyes are pyridyl rhodanines, given in formula (IV).



(IV)

Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are, i.a., heterocyclic mercapto compounds containing at least one electronegative substituent as described, e.g., in US-P 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described, e.g., in US-P 2,933,390 and US-P 3,635,721, aromatic organic acid/formaldehyde condensation products as described, e.g., in US-P 3,743,510, cadmium salts, and azaindene compounds.

The ratio of gelatin to silver halide is determined at the stage of precipitation and/or by further addition of gelatin at the redispersion stage or later. If added, it is preferred, to make the emulsion(s) comprising silver halide tabular grains ready for coating by addition to the emulsion(s) of an amount of hydrogen-bridge forming polymer in such an amount that the ratio of hydrogen bridge-forming polymer to silver halide expressed as silver nitrate is comprised between 0.05

and 0.40 and, more preferably, between 0.15 and 0.30. Otherwise, if silica is present as a binder in the preparation step of said emulsions, a preferred ratio of silica to silver halide expressed as silver nitrate is comprised between 0.03 and 0.3 and, more preferably, between 0.05 and 0.15 as has been disclosed in EP-A 0 528 476. The binder added in addition before coating of hydrophilic colloidal layers on a suitable support is determining the physical properties of the resulting coated film material. Properties as, e.g., dimensional stability, scratchability, curl, pressure sensitivity and sludge formation after processing are highly dependant on the choice of the protective colloid. Gelatin is the most universal protective colloid used in photography, but alternatives, like e.g. colloidal silica and/or synthetic clays are not excluded.

Embedded in a photographic material the silver halide tabular crystals prepared according to this invention are surrounded by colloidal silica if said colloidal silica is used in the precipitation step, serving as an extremely useful protective colloid. An especially advantageous effect resulting therefrom is the better resistance of the coated material to pressure phenomena. Emulsion layers in accordance with the present invention, and more particularly thin emulsion layers, are showing remarkable improvements concerning both resistance to stress and rapid processability compared to conventional emulsions prepared in gelatinous medium.

Thin coated layers obtained by coating lower amounts of binder, make this failure become worse, especially for materials coated from layers having thin tabular silver halide grains. If no silica sol is used as a binder in the precipitation of tabular silver halide emulsions, it is still possible to get a comparably improved resistance to stress if in at least one emulsion layer at least one synthetic clay is present as an additive as has been disclosed in EP-A 0 644 455, which is incorporated herein by reference.

As the ratio by weight of gelatin to silver halide decreases more pronounced pressure marks can be expected. Nevertheless as a result of the protective action of the adsorbed silica, if used in the precipitation step and/or synthetic clay used as a coating additive, much less pressure sensitivity appears.

To the emulsion(s) comprising silver halide tabular grains prepared in accordance with the present invention may be added compounds preventing the formation of fog or stabilizing the photographic characteristics prior to, during, or after the chemical ripening thereof or during the production or storage of photographic elements or during the photographic treatment thereof. Mixtures of two or more of these compounds can be used.

Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are the compounds described in Research Disclosure N° 17643 (1978), Ch.VI.

The silver halide emulsions prepared in accordance with the present invention can be used to form one or more silver halide emulsion layers coated on a support to form a photographic silver halide element according to well known techniques.

Two or more types of emulsions comprising silver halide tabular grains that have been prepared similarly or differently according to the method of this invention can be mixed in at least one emulsion layer for forming a photographic emulsion for use in accordance with the present invention.

The photographic element of the present invention may comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g higher contrast, sensitization, and development acceleration.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-P's 3,038,805; 4,038,075 and 4,292,400 and in EP-A's 0 634 849 and in EP-Application 94200639, filed March 11, 1994.

The photographic element of the present invention may further comprise various other additives such as, e.g., compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents, hardeners, and plasticizers as described below.

In accordance with this invention a light-sensitive photographic material is provided, having a support and, on at least one side thereof, at least one hydrophylic colloid layer including at least one light-sensitive silver halide emulsion layer characterised in that said light-sensitive layer comprises at least one of said emulsions having spectrally sensitized tabular grains as defined.

The layers of the photographic element, especially when the binder therein used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type, e.g., 1,3-vinylsulphonyl-2-propanol, bis-(vinyl sulphonyl)-methane, chromium salts e.g. chromium acetate and chromium alum, aldehydes, e.g., formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds, e.g., dimethylolurea and methyloldimethylhydantoin, dioxan derivatives, e.g., 2,3-dihydroxy-dioxan, active vinyl compounds, e.g., 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds, e.g., 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids, e.g., mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US-P 4,063,952 and with the onium compounds as disclosed in EP-A 0 408 143.

The emulsion may be coated on any suitable substrate such as, preferably, a thermoplastic resin, e.g., polyethyleneterephtalate or a polyethylene coated paper support. The support of the photographic material may be opaque or transparent, e.g., a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an Alpha-olefin polymer, e.g, a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support, e.g., cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer which can contain water insoluble particles such as silica or titanium dioxide.

Suitable additives for improving the dimensional stability of the photographic element may be added, i.a., dispersions of a water-soluble or hardly soluble synthetic polymer, e.g., polymers of alkyl (meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, α-β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

Plasticizers suitable for incorporation in the emulsions according to the present invention are, e.g., glycol, glycerine, or the latexes of neutral film forming polymers including polyvinylacetate, acrylates and methacrylates of lower alkanols, e.g, polyethylacrylate and polybutylmethacrylate.

Suitable UV-absorbers are, i.a., aryl-substituted benzotriazole compounds as described in US-P 3,533,794, 4-thiazolidone compounds as described in US-P's 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-P 4,045,229, and benzoxazole compounds as described in US-P 3,700,455.

In general, the average particle size of spacing agents is comprised between 0.2 μm and 10 μm. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US-A 4,614,708.

The photographic material can contain several non-light sensitive layers, e.g., a protective antistress topcoat layer, one or more backing layers, and one or more intermediate layers eventually containing filter- or antihalation dyes that absorb scattering light and thus promote the image sharpness, although for the blue to ultra-violet sensitized material the problem will be less than for green- and/or red-sensitised materials. Suitable light-absorbing dyes used in these intermediate layers are yellow dyes described in, e.g., US-P's 4,092,168 and 4,311,787 and in DE 2,453,217. When using dyes in such an intermediate layer between the emulsion layers and the support there will be only a small negligable loss in sensitivity but in rapid processing conditions decolouration of the filter dye layers may form a problem. Therefor it should be recommended to decrease the thickness of the whole coated layer packet resulting in shorter drying times after washing in the processing cycle. Alternatively the use of intermediate layers situated between emulsion layer(s) and support, reflecting the fluorescent light emitted by the screens in the case of radiographic film-screen combinations may bring a solution.

The photographic tabular silver halide emulsions can be used in various types of photographic elements such as, i.a., in photographic elements for so-called amateur and professional photography, for graphic arts, diffusion transfer reversal photographic elements, low-speed and high-speed photographic elements, X-ray materials, micrografic materials, etc..

In a preferred embodiment the photographic silver halide emulsions are used in X-ray materials. In X-ray photography a material with a single or a duplitized emulsion layer coated on one or both sides of the support may contain tabular silver halide emulsions spectrally sensitised according to the invention. By using duplitized emulsions differing in photographic speed by at least 0.15 log E a gain in cross-over exposure in double side coated materials can be obtained.

According to this invention a light-sensitive silver halide emulsion is provided, comprising tabular grains spectrally sensitized by the method disclosed hereinbefore, as well as a photographic material comprising a support and on at least one side of said support at least one hydrophilic colloid layer and at least one photosensitive layer comprising at least one photographic silver halide emulsion with tabular grains spectrally sensitized as defined and wherein the total amount of silver coated on one side of said support, expressed as the equivalent amount of silver nitrate, is less than 10 g/m^2, more preferably less than 7 g/m^2 and still more preferably less than 5.5 g/m^2. Further according to this invention the time to dissolve the coated layers of said material, determined by the method disclosed hereinafter, is not less than 45 minutes and, more preferably, not less than 60 minutes.

The said "time" means "the period of time from the moment when a silver halide photographic light-sensitive material cut into a sample having a size of 1 cm x 2 cm is dipped into an aqueous solution of 1.5 % by weight of NaOH at 50°C, until the moment when at least one of the silver halide emulsion layers constituting the said material starts to dissolve".

In the case of color photography the material contains blue, green and red sensitive layers each of which can be single coated, but generally consist of double or even triple layers. Besides the light sensitive emulsion layer(s) the photographic material may contain several light-insensitive layers, e.g., a protective antistress layer, one or more backing layers, one or more subbing layers, one or more intermediate layers, e.g., filter layers and even an afterlayer containing e.g. the hardening agent(s), the antistatic agent(s), filter dyes for safety-light purposes, etc.

One or more backing layers can be provided at the non-light sensitive side of the support of materials coated with at least one emulsion layer at only one side of the support. These layers which can serve as anti-curl layer can contain, e.g., matting agents like silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g., titanium oxide and the usual ingredients like hardeners and wetting agents.

The photographic material containing blue-sensitized tabular grains according to the present invention can be image-wise exposed by any convenient radiation source in accordance with its specific application. Particularly a radiographic screen-film combination comprising at-least one X-ray intensifying screen emitting blue and/or ultraviolet light, more specifically in the 400 to 500 nm range, in operative association with the material according to this invention is preferred. Particularly useful X-ray intensifying screens emitting blue and/or ultraviolet radiation have been described in WO93/11457 and 93/11458, which are incorporated herein by reference. Further references are US-P's 4,524,016; 4,959,174; 5,077,145; 5,064,729; 5,069,982; 5,250,365; 5,250,366 and 5,310,505 and EP-A's 0 592 724 and 0 520 094.

Of course processing conditions and composition of processing solutions are dependent from the specific type of photographic material in which the tabular grains prepared according to the present invention are applied. For example, in a preferred embodiment of materials for X-ray diagnostic purposes said materials may be adapted to rapid processing conditions, including the steps of developing, fixing, rinsing and drying. Preferably an automatically operating processing apparatus is used provided with a system for automatic regeneration of the processing solutions The forehardened material may be processed using one-part package chemistry or three-part package chemistry, depending on the processing application determining the degree of hardening required in said processing cycle. Within the scope of this invention applications within total processing times of up to 30 s are possible, whereas applications up to 90 seconds are known as common praxis. From an ecological point of view it is even possible to use sodium thiosulphate instead of ammonium thiosulphate and to reduce the regeneration amounts of developer and fixer.

The following examples are illustrative for the invention, without however limiting it thereto. In said examples all percentages are percentages by weight unless otherwise stated.

EXAMPLES

All tabular grains were precipitated using the double jet technique with control of the pAg value, said value being defined as the negative logarithm of the silver ion concentration.

After precipitation, every example was analysed using shadowed carbon replicas obtained with an electron microscope. For each example a minimum of hundred grains were measured and the following characteristics were then calculated :

- the number of tabular grains were calculated, a tabular grain being defined as a grain with two parallel main planes and a ratio between the diameter and the thickness of the grains of at least 2, with
- the diameter being the diameter of a circle having an equivalent projective surface area of the grain and
- the thickness being the distance between the main planes of the flat tabular crystals

A characterization of the crystal population of an emulsion was given by

- average diameter: calculated as the average by number from the diameters of the tabular grains.
- coefficient of variation of the tabular grains: calculated as the ratio between the standard deviation of the average diameter and the average diameter
- average thickness: calculated as the average by number from the distance between the main planes measured for all crystals
- aspect ratio: as the ratio between the mean calculated diameter and the mean calculated thickness defined hereinbefore
- percentage of the total projective surface: part of the total projective area covered by the tabular grains in percentage.

For all examples three solutions were used during the precipitation:
Solution 1: 1.5 liter of an aqueous solution containing 500 grams of silver nitrate.
Solution 2: 1.5 liter of an aqueous solution containing 350 grams of potassium bromide.
Solution 3 : 1.5 liter of an aqueous solution containing 341 grams of potassium bromide and 12.2 grams of potassium iodide.

Example 1

Emulsion No. 1 (comparative):

As a comparative emulsion a photographic silver iodobromide emulsion containing 2.0 mole % of silver iodide was prepared by a conventional single jet method in a vessel containing 40 g of phthaloyl gelatin. The ammoniacal silver nitrate solution was held at 42°C as well as the emulsion vessel, containing the halide salts.
At a constant rate of 300 ml per minute the precipitation time was ended after 10 minutes and followed by a physical ripening time of 40 minutes. After that time an additional amount of 20 g of gelatin was added. The obtained emulsion was of an average grain diameter of 0.62 μm and contained approximately 90 g of silver nitrate per kg of the dispersion after addition of 3 moles of silver nitrate.

After addition of sulphuric acid to a pH value of 3.5 stirring was stopped and after sedimentation the supernatant liquid was removed. The washing procedure was started after a scrape-rudder was installed and after addition of polystyrene sulphonic acid in the first turn to get a quantitative flocculate without silver losses.

During the redispersion of the emulsion 150 g of gelatin were added so that the weight ratio of gelatin to silver nitrate was 0.42, the emulsion containing an amount of silver bromoiodide equivalent with 190 g of silver nitrate pro kg.

The emulsion crystals were chemically ripened with sulphur and gold at 47°C for 4 hours to get an optimized relation between fog and sensitivity.

Emulsion No. 2 (invention):

The preparation steps were a nucleation and a first neutralization step, followed by a first growth step, a second neutralization step and a second growth step.

Nucleation step:

41.3 ml of solutions 1 and 2 were introduced into a reaction vessel in 28 seconds using the double jet technique. Said reaction vessel initially contained 2.16 liter of distilled water at 45°C, 12.6 grams of potassium bromide and 12.5 grams of gelatin. After one minute the reaction temperature of this mixture was raised to 70°C in 20 minutes and 47.5 grams of phthalated gelatin in 475 ml destilled water were added. After 10 minutes the neutralization step was started.

Neutralization step:

21.7 ml of solution 1 were added to the reaction vessel at a rate of 7.5 ml per minute to reach a pBr value of 1.63, whereafter the first growth step was started.

First growth step:

A double jet precipitation was started using solutions 1 and 2 which continued for 40 minutes 51 seconds. During this precipitation, the pBr value was kept constant at 1.63. The flowing rate of solution 1 was 7.5 ml per minute at the start, linearly increasing to 26.7 ml per minute at the end of the precipitation. Thereafter the second neutralisation phase was started.

Second neutralization step:

45.8 ml of solution 1 was added at a rate of 7.5 ml per minute so that a pBr of 2.77 was obtained. The precipitation was then continued by a second growth step.

Second growth step (during which 47.0 % of the total amount of $AgNO_3$ was used):

704 ml of solution 1 was injected in the reaction vessel at a rate of 7.5 ml per minute at the start linearly increasing to 37.5 ml per minute at the end of the precipitation. The pBr was kept constant at 2.77 using solution 2 for the first 8 minutes and 51 seconds, followed by the replacement of solution 2 by solution 3 for the rest of the precipitation.
The tabular grain emulsion obtained, had the following characteristics, measured with electron microscopic techniques:

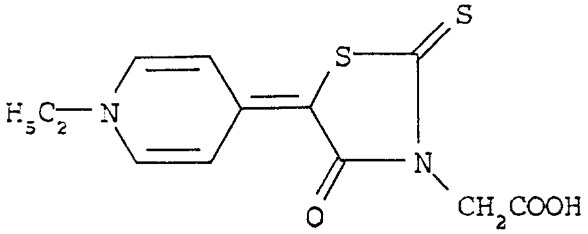
- average diameter: 1.26 µm
- coefficient of variation of the tabular grains : 0.37
- average thickness: 0.15 µm
- aspect-ratio : 8.9
- percentage of total projective surface: 99 %.

Washing and dispersing procedure.

After the emulsion precitation was ended the pH value was lowered to 3.5 with diluted sulphuric acid and the emulsion was washed using demineralized water of 11°C. At 45°C 160 grams of gelatin were added and the values of pH and pAg at 40°C were adjusted to 5.5 and 8.15.

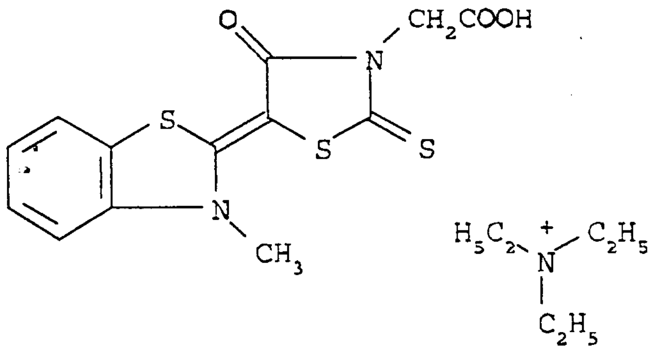
Sensitization

The emulsion was optimally sulphur and gold sensitized in the presence of sodium thiocyanate, toluene thiosulphinic acid, sulphite ions and stabilizing compound phenylmercaptotetrazol in the presence of the blue spectral sensitizer, according to the formula (V) in an amount of 2.1 mmole per mole of silver bromoiodide.



(V)

Emulsion No. 3 : same emulsion as emulsion No. 2 but no blue sensitising dye was used in the chemical ripening step.
Emulsion No. 4 : same emulsion as emulsion No. 2 but the blue sensitising dye, according to the formula (V) was not added in the chemical ripening step but after said step and before addition of further coating solutions (see further).
Emulsion No. 5 : same emulsion as emulsion No. 4 but another blue sensitising dye, according to the formula (VI) was added after the chemical ripening step and before addition of further coating solutions (see further).
Emulsion No. 6 : same emulsion as emulsion No. 2 but another blue sensitising dye, according to the formula (VI) was added before chemically ripening the emulsion grains.

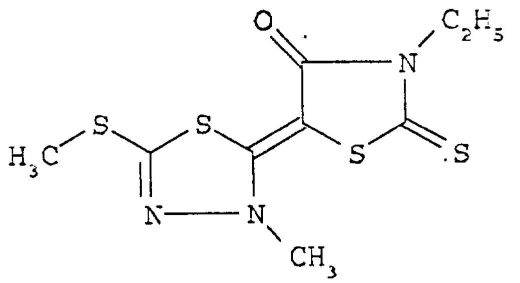


(VI)

Emulsion No. 7 : same emulsion as emulsion No. 6 but from the blue sensitising dye, according to the formula (VI), an amount of 30 % in excess was added versus the amount added to the emulsion No. 6 before chemically ripening the emulsion grains.

Emulsion No. 8 : same emulsion as emulsion No. 2 but an amount per m^2 of 0.25 g of silica sol (Kieselsol 500, trademarked product from Bayer AG) was added per m^2 to the emulsion layer before coating.

Emulsion No. 9 : same emulsion as emulsion No. 2 but another blue sensitising dye, according to the formula (VII), without solubilizing group, was added in the same amount before chemically ripening the emulsion grains.



(VII)

Emulsion Coatings (expressed per litre after addition of demineralized water in order to reach a concentration corresponding to about 200 g of silver nitrate per liter of coating solution).

- 785 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as antifogging agent and stabilizer,
- 39 mg of phloroglucin as hardening accelerator
- 2.68 g of resorcin as hardening agent

A protective coating composition was prepared containing per liter the following ingredients in demineralized water:

- 35.4 g of an inert gelatin
- 37 g of silica sol with silica particles having an average diameter of from 7 to 10 nm
- 20 g of an aqueous dispersion of matting agent with a particle size diameter of 2 µm comprising 3.2% of polymethylmethacrylate and 10% of gelatin
- 225 mg of chromium acetate as a hardening agent
- 300 mg of ammoniumperfluoro-octanoate (FC143, trade name product from 3M) and 750 mg of N-polyoxyethylene-N-ethyl-perfluoro-octane-sulfonamide (FC170C, trade name product from 3M) as surfactants
- 1500 mg of phenol as preserving agent
- 1000 mg of Mobilcer Q from MOBIL OIL as a lubricant

  Formaldehyd was added as a hardening agent.

The solutions for the emulsion coating and for the protective coating were coated simultaneously on both sides of a polyethylene terephthalate film support having a thickness of 175 µm, together with a protective layer containing 1.1 g gelatine per m^2 per side

Exposure, sensitometric and densitometric data:

Samples of these coatings were exposed to visible light coming from projection lamps (130V; 250W) of an exposure voltage of 90V during 0.1 s at a distance of 1.8 m from the film, through a continuously varying carbon-coated wedge (wedge constant 0.15), a densitometric filter with a density of 0.30 and a "Corning filter 5850" as a blue filter with a density 2.64 (measured with a Macbeth TR 924 densitometer). The exposed samples were processed during the 90 seconds cycle described below. The density as a function of the light dose was measured and therefrom were determined the following parameters:

- fog level (with an accuracy of 0.001 density; figure given =1000 times fog D),
- the relative speed S at a density of 1 above fog (the sample with the comparative emulsion was adjusted to a relative speed value of 100),
- the contrast, calculated between the densities 0.25 and 2.0 above fog.
- the amount of silver coated, expressed as the equivalent amount of $AgNO_3$ (in g/m^2)
- covering power (CP): ratio of maximum density and amount of silver developed in the area of maximum density.
- dye stain (NO=no dye stain; ACC=acceptable; YES= unacceptable)
  The processing occurred in a glutaraldehyde containing hydroquinone/1-phenyl-3-pyrazolidinone developer marketed by Agfa-Gevaert N.V. under the trade name G138 having a high activity.

Processing conditions and composition of developers.

- processing machine : CURIX 402 (Agfa-Gevaert trade name) with the following time (in seconds (sec.)) and temperature (in °C)
  characteristics:

loading	3.4 sec.
developing	23.4 sec./ 35°C high or low activity developer
cross-over	3.8 sec.
fixing	15.7 sec./ 35°C in fixer AGFA G334 (trade name)
cross-over	3.8 sec.
rinsing	15.7 sec./ 20°C.
drying	32.2 sec. (cross-over time included)
total time	$\overline{98.0}$ sec.

Table 1

Em. No.	Fog	Speed*	Contrast	$AgNO_3/m^2$	CP	STAIN
1	20	100	2.66	8.44	40	NO
2	24	108	3.04	5.51	66	NO
3	6	151	3.43	5.57	62	NO
4	29	155	3.09	5.49	60	NO
5	10	136	2.83	5.52	62	ACC
6	10	133	3.22	5.62	66	YES
7	11	113	3.31	5.51	68	YES
8	21	108	3.10	5.52	67	NO
9	42	125	2.45	5.50	65	NO

*Speed (see Table 1): as the amount of light needed to reach a density of 1.00 above fog and support density is lower for the more light-sensitive materials the sensitivity is higher for lower values. Expressed as in Table 1 in 100 times log exposure this means that every decrease with a value of 30 is indicative for a material with a sensitivity that is twice as high.

For the materials coated from the emulsion Nos. 2 to 9, the time interval as defined hereinbefore till the moment when at least one of the silver halide emulsion layers constituting the said materials started to dissolve, expressed in minutes, was determined. The dissolution time for each sample was between 60 and 65 minutes.

It can be concluded from Table 1 that photographic materials, according to this invention, comprising tabular grains spectrally sensitized with a blue dye in the chemical ripening step, it is possible to get, even with remarkably lower amounts of silver bromoiodide coated, an acceptable speed, contrast and fog, as well as an obviously enhanced covering power and, moreover, no dye stain.

If a spectrally sensitizing dye, differing from the preferred type according to this invention is used (see Em. No. 9), or if spectral sensitization is not applied during the chemical sensitisation step or before, a remarkable loss in speed occurs.

Moreover it has been proved that considerably better preservation characteristics are obtained: a lower increase in minimum density and less decrease in speed.

The same coatings were exposed in the same way as disclosed hereinbefore and processed during the 38 seconds processing cycle in the processing machine CURIX HT530 (Agfa-Gevaert trademarked name) with the following time (in seconds) and temperature (in °C) characteristics:

loading	0.2 sec.
developing	9.3 sec. 35°C in developer described below
cross-over	1.4 sec.
rinsing	0.9 sec.
cross-over	1.5 sec.
fixing	6.6 sec. 35°C in fixer described below
cross-over	2.0 sec.
rinsing	4.4 sec. 20°C
cross-over	4.6 sec.
drying	6.7 sec.
total	37.6 sec.

The processing was run in a developer and fixer solution made from concentrated stock solutions, free from hardening agents as illustrated hereinafter.

Composition of Developer:

-concentrated part :	
water	200 ml
potassium bromide	12 grams
potassium sulphite (65% solution)	249 grams
ethylenediaminetetraacetic acid, sodium salt,trihydrate	9.6 grams
hydroquinone	106 grams
5-methylbenzotriazole	0.076 grams
1-phenyl-5-mercaptotetrazole	0.040 grams
sodiumtetraborate (decahydrate)	70 grams
potassium carbonate	38 grams
potassium hydroxide	49 grams
diethylene glycol	111 grams
potassium iodide	0.022 grams
4-hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidinone	3 grams
Water to make 1 liter pH adjusted to 11.15 at 25°C with potassium hydroxide.	

For initiation of the processing one part of the concentrated developer was mixed with 3 parts of water.
No starter was added.
The pH of this mixture was 10.30 at 25°C.

Composition of Fixer:

-concentrated part :	
ammonium thiosulfate (78% solution)	661 grams
sodium sulphite	54 grams
boric acid	25 grams
sodium acetate-trihydrate	70 grams
acetic acid	40 grams
water to make 1 liter pH adjusted with acetic acid to 5.30 at 25°C	

To make this fixer ready for use one part of this concentrated part was mixed with 4 parts of water. A pH of 5.25 was measured at 25°C.

In Table 2 the figures obtained for the same variable data as in Table 1 are summarized.

Table 2

Em. No.	Fog	Speed*	Contrast	$AgNO_3/m^2$	CP	STAIN
1	19	100	2.40	8.44	39	NO
2	15	108	2.87	5.51	64	NO
3	5	150	3.21	5.57	60	NO
4	20	161	2.68	5.49	52	NO
5	8	143	2.56	5.52	57	ACC
6	5	136	3.01	5.62	64	YES
7	6	117	3.14	5.51	67	YES
8	14	108	2.92	5.52	67	NO
9	31	127	2.40	5.50	65	NO

The same conclusion as in Table 1 can be drawn from the data summarized in Table 2.

Example 2

Emulsion No. 2 (invention) from Example 1 was taken and experiments were performed during chemical sensitization in the presence of triphenylphosphorselenide as a selenium ion providing compound.

In Table 3, the most relevant sensitometric results are given, said results being given as a function of variations in amounts of sulphur and gold, added in combination with the said triphenylphosphorselenide compound. Amounts of sulphur (S), selenium (Se) and gold (Au) (expressed in µmole per mole of silver) are also summarized in Table 3. Coatings (emulsion, protective layer) were performed just as described in Example 1. Said coatings were further exposed and processed in a 98 seconds (CURIX 402) processing cycle in the corresponding processing solutions as mentioned in Example 1 hereinbefore. In Table 3, additional results are also given of sensitometric results obtained with the same materials after a preservation time of 1.5 months at room temperature.

Table 3

Em.	Fog	Speed	Contr	S	Se	Au	Fog**	Speed**	Contr
2/1	57	100	2.65	12.6	0	4.4	50	101	2.53
2/2	173	89	1.99	0	6.8	4.4	161	90	1.91
2/3	136	71	2.28	0	6.8	8.8	139	74	2.20
2/4	43	102	2.13	2.1	3.9	4.4	43	102	2.03
2/5	36	89	2.57	5.5	2.0	4.4	34	89	2.58
2/6	39	91	2.66	8.4	1.0	4.4	35	92	2.65

** after preservation of the material during 1.5 months at room temperature.

From the results in Table 3 it can be concluded that chemical ripening in the presence of a gold and a selenium ion providing compound but in the absence of a sulphur ion providing compound gives a good speed level but makes fog rise.

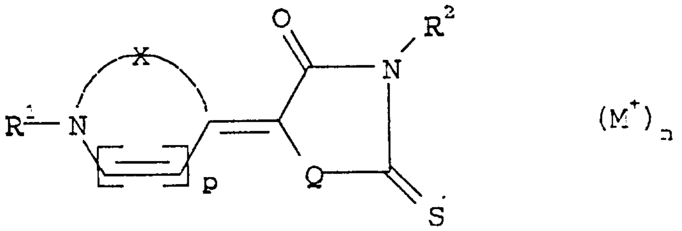
Combination of sulphur, selenium and gold providing compounds gives very low (even decreased) fog levels and a remarkably increased speed level!

Results obtained after preservation of the material are showing very good, preservation characteristics for the materials having sulphur, selenium and gold providing compounds added in the chemical ripening step.

Another favourable aspect which has been established is that the blue sensitized tabular grains chemically ripened with sulphur, selenium and gold ion providing compounds are less sensitive to darkroom light than the corresponding grains, ripened with selenium and gold or with sulphur and gold providing compounds alone. "Fog"-density differences between an exposed and unexposed part of a film material measured after processing as described hereinbefore, said exposed part being exposed to darkroom light during 3 minutes with a darkroom filter GBX3, so that the light intensity at the film was 36 lux were 50, 161, 139, 43, 34 and 35 for the materials corresponding to Em. Nos. 2/1-2/6.

Claims

1. Method for manufacturing a tabular silver halide emulsion wherein tabular silver halide grains having an aspect ratio of at least 2:1, an average crystal diameter between 0.3 µm and 3.0 µm and an average thickness of less than 0.50 µm account for at least 50 % of the total projective surface area of said grains, and wherein said method comprises the steps of precipitating said grains, spectrally sensitizing and chemically ripening, characterized by adding to the emulsion before and/or during chemically ripening at least one spectrally sensitizing dye corresponding to the general formula (I)



(I)

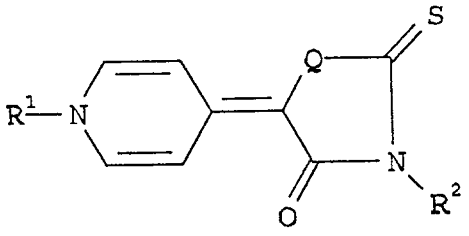
wherein
X represents the atoms, necessary to form a heterocyclic 5- or 6-membered ring;
Q represents S, NR^3, O, or -(C=O)-N(R^4)-;
M$^+$ represents a kation;
n equals 0, 1, or 2;
p equals 0 or 1;
R^1, R^2, R^3 and R^4 each independently represent a substituted or unsubstituted C$_1$-C$_5$ alkyl chain, with the proviso that at least one of R^2, R^3 and R^4 has a solubilizing group or a latent solubilizing group.

2. Method according to claim 1, wherein the average thickness of the tabular silver halide grains is less than 0.30 µm.

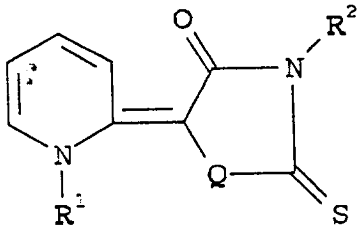
3. Method according to claim 1 or 2, wherein in said dye corresponding to the general formula (I), the alkyl chain containing at least one solubilizing group corresponds to one of the following formulae:
$(CH_2)_mSO_3^-$ or $(CH_2)_mN(R)SO_3^-$ wherein m equals 1, 2, 3 or 4, and wherein R has the same meaning as R^1 to R^4;
$(CH_2)_2CH(Y)SO_3^-$ wherein Y represents CH_3-, -Cl or -OH;
$(CH_2)_qOSO_3^-$ wherein q equals 2 or 3;
$(CH_2)_rCO_2^-(H^+)$ wherein r equals 1, 2 or 3;
$(CH_2)_sSO_2^-(CH_2)_tH$ wherein s equals 2 or 3 and t equals 1 or 2;
$-(CH_2)_x$-Phen-W, wherein W represents $-COO^-$ or SO_3^-;
Phen represents a phenyl group which is further substituted or unsubstituted, and x equals 1, 2, 3 or 4.

4. Method according to claim 1 or 2, wherein in said dye corresponding to the general formula (I), the alkyl chain containing at least one latent solubilizing group corresponds to the formula $(CH_2)_{m'}$-(C=O)-O-CH_2-(C=O)-CH_3, wherein m' is an integer having a value of from 1 to 5.

5. Method according to any of claims 1 to 4, wherein said dye corresponds to the formula (II) or (III)



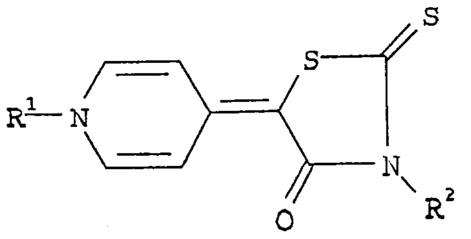
$(M^+)_n$ (II)



$(M^+)_n$ (III)

wherein Q, M^+, n, R^1 and R^2 have the same meaning as in claim 1.

6. Method according to any of claims 1 to 5, wherein said dye corresponds to the formula (IV)

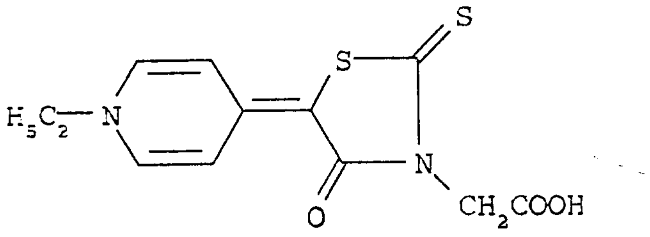


$(M^{-})_n$

$(M^+)_n$ (IV)

wherein R^1, R^2, n and M^+ have the same meaning as in claim 1.

7. Method according to any of claims 1 to 6, wherein said dye corresponds to the formula (V)



(V)

8. Method according to any of claims 1 to 7, wherein said grains have an average aspect ratio of at least 5:1.

9. Method according to any of claims 1 to 8, wherein chemical ripening of said blue sensitized tabular grains proceeds in the presence of combinations of sulphur, selenium and gold ion providing compounds.

10. A light-sensitive silver halide emulsion comprising tabular grains prepared according to the method of any of claims 1 to 9.

11. A light-sensitive silver halide photographic X-ray material comprising a support, at least one hydrophilic colloid layer on at least one side of said support and at least one photosensitive layer comprising at least one silver halide photographic emulsion according to claim 10, wherein the total amount of silver coated per side, expressed as the equivalent amount of silver nitrate is less than 10 g/m^2 and wherein the time to dissolve the coated layers of said material, determined by the method disclosed herein, is not less than 45 minutes.

12. A radiographic screen-film combination comprising at least one X-ray intensifying screen emitting blue and/or ultraviolet light in operative association with a material according to claim 11.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 20 3024

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	JP-A-01 187 544 (FUJI PHOTO FILM CO LTD) 26 July 1989 * the whole document * & Patent Abstracts of Japan, vol.13, no.475 (P-950) ---	1-11	G03C1/005 G03C1/22
X	JP-A-04 295 842 (KONICA CORP.) 20 October 1992 * column 13, line 10 - line 30 * & Patent Abstracts of Japan, vol.17, no.107 (P-1496) ---	1-11	
X	JP-A-05 224 347 (KONICA CORP.) * compound [2-3] on p.(9) / col.15/16 * & Patent Abstracts of Japan, vol.17, no.669 (P-1657) ---	1-11	
D,A	EP-A-0 404 142 (FUJI PHOTO FILM CO.) * page 17, line 10 - line 30; claims * ---	1-11	
A	EP-A-0 622 665 (KONICA CORP.) * page 18, line 14 - line 20; claims * ---	1-11	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D,A	EP-A-0 300 382 (EASTMAN KODAK COMPANY) * page 2, line 22; claim 2 * -----	1-11	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 February 1996	Buscha, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

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