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(54) **High-contrast photographic elements with improved maximum density**

Photographische Hochkontrastelemente mit verbesserter Maximaldichte

Eléments photographiques à contraste élevé et à densité maximale améliorée

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EP-A- 0 562 615 **US-A- 4 933 272**
US-A- 5 061 595 **US-A- 5 283 169**

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DescriptionFIELD OF THE INVENTION

5 **[0001]** This invention relates in general to photography and in particular to novel black-and-white silver halide photographic elements. More specifically, this invention relates to high-contrast room-light-handleable silver halide photographic elements which are especially useful in the field of graphic arts.

BACKGROUND OF THE INVENTION

10 **[0002]** High-contrast room-light-handleable black-and-white silver halide photographic elements are well known and widely used in graphic arts applications. The term "room-light-handleable" is intended to denote that the material can be exposed to a light level of 200 lux for several minutes without a significant loss in performance.

15 **[0003]** The silver halide emulsions utilized in high-contrast room-light-handleable photographic elements are slow speed emulsions, with the desired slow speed typically being achieved by the use of small grain sizes and by the doping of the silver halide grains with appropriate doping agents that control photographic speed. The incorporation of filter dyes in an overcoat layer of the photographic element to absorb unwanted light and decrease photographic speed is also a commonly employed technique.

20 **[0004]** Photographic silver halide emulsions comprised of radiation-sensitive silver halide grains exhibiting a face centered cubic crystal lattice structure internally containing a nitrosyl or thionitrosyl coordination ligand and a transition metal chosen from groups 5 to 10 inclusive of the periodic table of the elements are described in McDugle et al, US-A-4,933,272. As disclosed in the '272 patent, these doping agents are useful in a wide variety of photographic elements and are especially useful in high-contrast room-light-handleable black-and-white photographic elements. In such elements, these doping agents are used in relatively high concentrations for the purposes of reducing speed and increasing contrast. However, use of such high concentrations tends to cause solarization and intermittency problems with consequent loss in maximum density. US-A-5,061,595 also describes the use of these dopants in graphic arts films.

25 **[0005]** US-A-5,283,169 describes the combination of transition metal-ligand dopants with compounds that provide room-light-handleability.

30 **[0006]** It is toward the objective of providing an improved high-contrast room-light-handleable black-and-white photographic element, which is doped in a manner that is effective to provide low speed and high contrast without encountering significant loss in maximum density, that the present invention is directed.

SUMMARY OF THE INVENTION

35 **[0007]** In accordance with this invention, a high-contrast room-light-handleable black-and-white silver halide photographic element that is especially adapted for use in the field of graphic arts is comprised of a support bearing a silver halide emulsion layer comprising fine-grain high-chloride radiation-sensitive silver halide grains exhibiting a face centered cubic crystal lattice structure internally containing a dopant comprised of a nitrosyl coordination ligand and a transition metal, the element characterized wherein the dopant is present in the grains in an amount of from 5×10^{-6} to 3×10^{-4} mol/mol of silver, at least 25 percent by weight of the total amount of the dopant within the grains being located within the outermost 90 percent of the total grain volume in order to reduce the effects of solarization and intermittency on the emulsion and thereby enhance the maximum density of the element.

40 **[0008]** It is preferred that at least 50 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume. In the most preferred embodiment of the invention, 100 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume.

45 **[0009]** Solarization is a well-known problem in the photographic arts. It refers to the phenomenon that when a silver halide emulsion is very heavily overexposed, the developable density begins to decrease. The principal cause of solarization is the destruction of the surface latent image by halogen liberated from the formation of the internal image.

50 **[0010]** Intermittency is also a well-known problem in the photographic arts. It refers to the phenomenon that the effect produced by an intermittent-exposure is, for equal energies, lower than the effect provided by a continuous exposure. The characteristic curve obtained with intermittent exposures has lower densities, especially at lower intermittency values.

55 **[0011]** More detailed information pertaining to both solarization and intermittency is available in standard textbooks pertaining to photography (see, for example, Photographic Materials And Processes by Leslie Stroebel, John Compton, Ira Current and Richard Zakia, Butterworth Publishers, 80 Montvale Avenue, Stoneham, MA 02180, 1986; James, The Theory of the Photographic Process, 4th Ed., MacMillan Publishing Co., 1977 and Introduction to Photographic Theory, by B. H. Carroll, G. C. Higgins and T. H. James, John Wiley & Sons, New York, N.Y. 1980).

5 [0012] In accordance with this invention, it has been discovered that utilizing specific doping agents in a manner in which at least 25 percent by weight of the total amount of dopant within the grains is located within the outermost 90 percent of the total grain volume eliminates or at least significantly reduces solarization and intermittency problems and thereby eliminates or at least significantly reduces the loss in maximum density attributable thereto. The dopant is introduced into the silver halide grains during precipitation thereof, typically in a manner which forms a band of dopant within the grain and the width and location of this band can be readily manipulated to achieve the desired objective of locating the dopant in the aforesaid manner. For example, the time at which introduction of dopant is started in the precipitation process and the duration of the run length over which the dopant is introduced can be selected to achieve this objective. The optimum width of the band, the optimum distance from the mid-point of the grain to the inner edge of the band and the optimum distance from the outer edge of the band to the surface of the grain will vary depending on such factors as the size of the grains, the halide content, the particular dopant utilized and the concentration of dopant.

15 DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 [0013] High-contrast room-light-handleable black-and-white photographic elements typically utilize fine-grain high-chloride emulsions. Thus, it is preferred that the grains utilized in this invention have a mean grain size of less than 0.4 μm , preferably less than 0.2 μm and most preferably less than 0.1 μm . It is also preferred that the grains utilized in this invention have a chloride content of at least 80 mole % and preferably at least 90 mole %. Most preferably, the grains are 100 percent chloride.

25 [0014] The high-contrast room-light-handleable photographic elements of this invention utilize certain dopants that comprise a nitrosyl coordination ligand. As shown by the working examples herein, locating the dopant so that at least 25 percent by weight of the total amount of dopant within the grains is located within the outermost 90 percent of the total grain volume results in elimination, or at least substantial reduction, of solarization and intermittency. This makes it possible to provide a room-light-handleable element with the highly desirable combination of low speed, high contrast and high maximum density (D_{max}).

30 [0015] The high-contrast room-light-handleable photographic elements of this invention can utilize any of the polymeric film supports known for use in the photographic arts. Typical of useful polymeric film supports are films of cellulose nitrate and cellulose esters such as cellulose triacetate and diacetate, polystyrene, polyamides, homo- and co-polymers of vinyl chloride, poly(vinylacetal), polycarbonate, homo- and co-polymers of olefins, such as polyethylene and polypropylene and polyesters or dibasic aromatic carboxylic acids with divalent alcohols, such as poly(ethylene terephthalate).

35 [0016] Polyester films, such as films of polyethylene terephthalate, have many advantageous properties, such as excellent strength and dimensional stability, which render them especially advantageous for use as supports in the present invention.

40 [0017] The polyester film supports which can be advantageously employed in this invention are well known and widely used materials. Such film supports are typically prepared from high molecular weight polyesters derived by condensing a dihydric alcohol with a dibasic saturated fatty carboxylic acid or derivatives thereof. Suitable dihydric alcohols for use in preparing polyesters are well known in the art and include any glycol, wherein the hydroxyl groups are on the terminal carbon atom and contain from 2 to 12 carbon atoms such as, for example, ethylene glycol, propylene glycol, trimethylene glycol, hexamethylene glycol, decamethylene glycol, dodecamethylene glycol, and 1,4-cyclohexane dimethanol. Dibasic acids that can be employed in preparing polyesters are well known in the art and include those dibasic acids containing from 2 to 16 carbon atoms. Specific examples of suitable dibasic acids include adipic acid, sebacic acid, isophthalic acid, and terephthalic acid. The alkyl esters of the above-enumerated acids can also be employed satisfactorily. Other suitable dihydric alcohols and dibasic acids that can be employed in preparing polyesters from which sheeting can be prepared are described in J. W. Wellman, U.S. Patent No. 2,720,503, issued October 11, 1955.

50 [0018] Specific preferred examples of polyester resins which, in the form of sheeting, can be used in this invention are poly(ethylene terephthalate), poly(cyclohexane 1,4-dimethylene terephthalate), and the polyester derived by reacting 0.83 mol of dimethyl terephthalate, 0.17 mol of dimethyl isophthalate and at least one mol of 1,4-cyclohexanedimethanol. U.S. Patent No. 2,901,466 discloses polyesters prepared from 1,4-cyclohexanedimethanol and their method of preparation.

[0019] The thickness of the polyester sheet material employed in carrying out this invention is not critical. For example, polyester sheeting of a thickness of from 0.05 to 0.25 millimeters can be employed with satisfactory results.

55 [0020] In a typical process for the manufacture of a polyester photographic film support, the polyester is melt extruded through a slit die, quenched to the amorphous state, oriented by transverse and longitudinal stretching, and heat set under dimensional restraint. In addition to being directionally oriented and heat set, the polyester film can also be subjected to a subsequent heat relax treatment to provide still further improvement in dimensional stability and surface

smoothness.

[0021] The photographic elements of this invention are high contrast materials with the particular contrast value, as indicated by gamma (γ), depending on the type of emulsion employed. Gamma is a measure of contrast that is well known in the art as described for example, in James, The Theory of the Photographic Process, 4th Ed., 502, MacMillan Publishing Co., 1977.

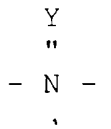
[0022] In addition to the fine-grain high-chloride silver halide emulsion layer, the elements of this invention can optionally contain additional layers, such as a backing layer, a protective overcoat layer, and an interlayer positioned between the emulsion layer and the overcoat layer.

[0023] As hereinabove described, fine-grain emulsions are utilized in this invention with the mean grain size preferably being less than 0.4 micrometers. Methods for determining the mean grain size of silver halide grains are well known in the photographic art. They are described, for example, in James, The Theory of the Photographic Process, 4th Ed., pages 100 to 102, MacMillan Publishing Co. (1977).

[0024] The silver halide emulsions utilized in this invention employ silver halide grains in which a doping agent as defined in U.S. 4,933,272 has been incorporated to control the speed. Such doping agents also serve to increase contrast. The doping agents are typically added during the crystal growth stages of emulsion preparation, for example, during initial precipitation and/or physical ripening of the silver halide grains.

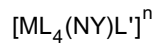
[0025] McDugle et al U.S. Patent 4,933,272, issued June 12, 1990 discloses silver halide emulsions comprised of radiation-sensitive silver halide grains exhibiting a face centered cubic crystal lattice structure internally containing a nitrosyl or thionitrosyl coordination ligand and a transition metal chosen from groups 5 to 10 inclusive of the periodic table of elements. These emulsions are adapted for use in the high-contrast room-light-handleable photographic elements of this invention by controlling the location of the dopant as hereinabove described.

[0026] The dopants contained within the silver halide grains are transition metal coordination complexes which contain one nitrosyl ligand. These ligands have the formula:



where Y is oxygen.

[0027] The transition metal coordination complexes satisfying the requirements of this invention are hexacoordination complexes represented by the formula:



where

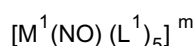
- M is a ruthenium, rhenium or iridium;
- L is bromide or cyanide;
- L' is L;
- Y is oxygen; and
- n is zero, -1, -2, or -3.

[0028] The present invention contemplates photographic emulsions in which the radiation-sensitive grains of a cubic crystal lattice structure internally contain a transition metal coordination complex, preferably a hexacoordination transition metal complex, containing at least one nitrosyl ligand for modifying photographic performance.

[0029] The nitrosyl ligands preferably account for one or two of the total ligands and aquo ligands, when present, also preferably account for only one or two of the ligands. Hexacoordinated transition metal complexes which include in addition to their nitrosyl ligands up to five bromide and/or cyanide ligands are specifically preferred.

[0030] The transition metal coordination complexes contemplated for grain incorporation in most instances exhibit a net ionic charge. One or more counter ions are therefore usually associated with the complex to form a charge neutral compound. The counter ion is of little importance, since the complex and its counter ion or ions dissociate upon introduction into an aqueous medium, such as that employed for silver halide grain formation. Ammonium and alkali metal counterions are particularly suitable for anionic hexacoordinated complexes satisfying the requirements of this invention, since these cations are known to be fully compatible with silver halide precipitation procedures.

[0031] Particularly preferred hexacoordinated complexes for use in this invention are those of the formula:



wherein

m is zero, -1, -2, or -3,

M¹ represents rhenium or ruthenium, and

L¹ represents one or a combination of bromide and cyanide ligands or a combination of these ligands with up to two aquo ligands.

[0032] In this invention, the concentration of dopant used is that which is sufficient to bring about the desired reduction in speed. The concentration is from 5×10^{-6} to 3×10^{-4} moles per silver mole.

[0033] In carrying out the present invention, the width of the dopant band can be readily controlled by controlling the duration of the interval over which dopant is added during the precipitation of the silver halide grains, with the width of the band varying directly with the duration of this interval. Also, the location of the dopant band can be readily controlled by selection of the time at which addition of dopant is begun. By delaying the start of dopant addition until the appropriate time in the precipitation, the dopant band can be located closer to the surface of the silver halide grain. Consider, for example, a silver halide grain precipitation process which requires a total of 15 minutes for completion. Starting the addition of dopant three minutes after precipitation begins, rather than one minute, will locate the dopant band nearer to the grain surface. Adding dopant for a total period of three minutes rather than one minute will result in a band of significantly greater width. In accordance with this invention, the location of the dopant within the grains is controlled to eliminate, or at least significantly reduce, solarization and intermittency effects.

[0034] In this invention, the location of the dopant is controlled in relation to grain volume. Since grain volume varies approximately in proportion to the cube of grain size, this needs to be taken into account in selecting the rate at which the dopant is added, the time at which addition of the dopant is started and the duration of the period of time over which the dopant is added.

[0035] In the growth of silver halide grains, the rate at which average particle size doubles is much more rapid at the beginning of the process than in the latter stages thereof. When the silver halide grain is very small, it increases rapidly in average particle size as a result of addition of a given amount of halide salt and silver salt, but when the grain is large addition of this same amount of halide salt and silver salt results in much less of a change in grain size. Thus, the addition of the dopant can commence fairly early in the grain growth process and still have the band of dopant located away from the core region of the grain.

[0036] In addition to the doped silver halide grains, the silver halide emulsions employed in this invention also contain a hydrophilic colloid that serves as a binder or vehicle. The proportion of hydrophilic colloid can be widely varied, but typically is within the range of from about 20 to 250 g/mole silver halide. The presence of excessive levels of hydrophilic colloid can reduce maximum image density and, consequently, contrast. Thus, for g values of 10 or more, the vehicle is preferably present at a level of less than 200 g/mole silver halide.

[0037] The hydrophilic colloid is preferably gelatin, but many other suitable hydrophilic colloids are also known to the photographic art and can be used alone or in combination with gelatin. Suitable hydrophilic colloids include naturally occurring substances such as proteins, protein derivatives, cellulose derivatives -- e.g., cellulose esters, gelatin -- e.g., alkali-treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives -- e.g., acetylated gelatin and phthalated gelatin, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar, arrowroot and albumin.

[0038] As hereinabove described, the silver halide grains utilized herein are high-chloride grains typically having a chloride content of at least 80 mole per cent. The remaining halide is typically bromide but can include a small amount of iodide.

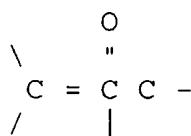
[0039] In addition to the hydrophilic colloid and the silver halide grains, the radiation-sensitive silver halide emulsion layers employed in this invention can include a polymer latex which serves to improve the dimensional stability of the film. Polymers usable in latex form for this purpose are very well known in the photographic art. The requirements for such a polymer latex are (1) that it not interact with the hydrophilic colloid such that normal coating of the emulsion layer is not possible, (2) that it have optical properties, i.e., refractive index, similar to that of the hydrophilic colloid, and (3) that it have a glass transition temperature such that it is plastic at room temperature. Preferably, the glass transition temperature is below 20°C.

[0040] The polymer latex useful in the present invention is an aqueous dispersion of a water-insoluble polymer. It is incorporated in an emulsion layer in an amount that is typically in the range of from 0.2 to 1.5 parts per part by weight of the hydrophilic colloid.

[0041] The synthetic polymeric latex materials referred to herein are generally polymeric materials which are relatively insoluble in water compared to water-soluble polymers, but have sufficient water solubility to form colloidal suspensions of small polymeric micelles. Typical latex polymeric materials can be made by rapid copolymerization with vigorous agitation in a liquid carrier of at least one monomer which would form a hydrophobic homopolymer. In certain preferred embodiments, from 1 to 30 percent, by weight, of units of monomer containing the water-solubilizing group is present in the copolymer product. Copolymers prepared by this method and analogous methods provide discrete micelles of the copolymer which have low viscosities in aqueous suspensions. Typical useful copolymers include interpolymers of acrylic esters and sulfoesters as disclosed in US-A-3,411,911, interpolymers of acrylic esters and sulfobetains as described in US-A-3,411,912, interpolymers of alkyl acrylates and acrylic acids as disclosed in US-A-3,287,289, interpolymers of vinyl acetate, alkyl acrylates and acrylic acids as disclosed in US-A-3,296,169, and interpolymers as disclosed in US-A-3,459,790. Polymeric latex materials can also be made by rapid polymerization with vigorous agitation of hydrophobic polymers when polymerized in the presence of high concentrations of surfactants which contain water-solubilizing groups. The surfactants are apparently entrained in the micelle and the solubilizing group of the surfactant provides sufficient compatibility with aqueous liquids to provide a dispersion very much like a soap. Generally good latex materials are also disclosed in US-A-3,142,568, US-A-3,193,386, US-A-3,062,674, US-A-3,220,844.

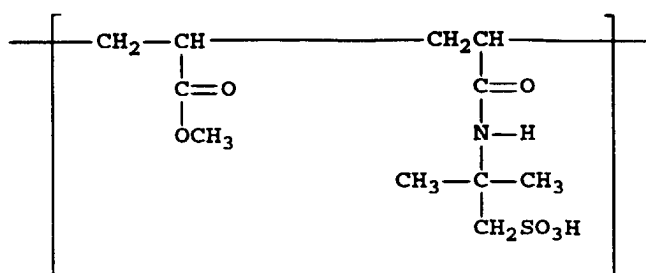
[0042] The synthetic polymeric latex materials are generally polymerized in a manner to produce micelles of about 1.0 μm average diameter or smaller to be highly useful in photographic emulsions and preferably the discrete micelles are less than 0.3 μm in average diameter. Generally, the micelles can be observed by photomicrographs when incorporated in gelatino emulsions, however, it is understood that some coalescing can occur when the emulsions are coated and dried.

[0043] In one embodiment, the latex polymers which can be used according to this invention are acrylic interpolymers, i.e., those interpolymers prepared from polymerizable acrylic monomers containing the characteristic acrylic group



[0044] Such polymers are conveniently prepared by the interpolymerization of an acrylic monomer with at least one dissimilar monomer which can be another acrylic monomer or some other different polymerizable ethylenically unsaturated monomer. It is, of course, understood that the acrylic interpolymers employed in the practice of this invention are compatible with gelatin and have a T_g (glass transition temperature) of less than 20°C. (T_g can be calculated by differential thermal analysis as disclosed in "Techniques and Methods of Polymer Evaluation", Vol. 1, Marcel Dekker, Inc., N.Y., 1966).

[0045] A particularly preferred polymer latex for use in a silver halide emulsion layer is poly(methylacrylate-co-2-acrylamido-2-methyl propane sulfonic acid) which is comprised of repeating units of the formula:



[0046] The thickness of the radiation-sensitive silver halide emulsion layer in the photographic elements of this invention is typically in the range of from 1 to 9 μm , and more preferably in the range of from 2 to 4 μm .

[0047] The total concentration of silver in the novel photographic elements of this invention is typically in the range of from 0.5 to 5.5 grams of silver per square meter, more preferably in the range of from 1.5 to 4.5 grams of silver per square meter, and most preferably in the range of from 2.5 to 3.5 grams of silver per square meter.

[0048] The novel photographic elements of this invention can include an overcoat layer containing a hydrophilic

colloid and a matting agent. The hydrophilic colloid can be selected from among those described above as being useful in the emulsion layer. Most preferably, the hydrophilic colloid in the overcoat layer is gelatin.

[0049] Discrete solid particles of a matting agent, typically having an average particle size in the range of from 1 to 5 μm and preferably in the range of from 2 to 4 μm , can be utilized in the overcoat layer. The matting agent is typically employed in an amount of from 0.02 to 1 part per part by weight of the hydrophilic colloid. Either organic or inorganic matting agents can be used. Examples of organic matting agents are particles, often in the form of beads, of polymers such as polymeric esters of acrylic and methacrylic acid, e.g., poly(methylmethacrylate), cellulose esters such as cellulose acetate propionate, cellulose ethers, ethyl cellulose, polyvinyl resins such as poly(vinyl acetate), styrene polymers and copolymers. Examples of inorganic matting agents are particles of glass, silicon dioxide, titanium dioxide, magnesium oxide, aluminum oxide, barium sulfate and calcium carbonate. Matting agents and the way they are used are further described in U.S. Patent Nos. 3,411,907 and 3,754,924.

[0050] Particles used as matting agents in the present invention can be of essentially any shape. Their size is typically defined in terms of mean diameter. Mean diameter of a particle is defined as the diameter of a spherical particle of identical mass. Polymer particles that are in the form of spherical beads are preferred for use as matting agents.

[0051] The thickness of the overcoat layer is typically in the range of from 0.2 to 1 μm , preferably in the range of from 0.3 to 0.6 μm and most preferably in the range of from 0.35 to 0.45 μm .

[0052] The side of the support opposite to the emulsion layer is typically coated with an antihalation layer whose function is to prevent light that passes through the film support from being reflected into the image-forming layer and thereby causing an undesired spreading of the image which is known as halation. The antihalation layer may in turn be overcoated with another layer which serves as a protective outermost layer. Alternatively, antihalation protection can be provided by incorporating a non-migrating dye in a layer under the emulsion layer.

[0053] As lithographic-type photographic elements, the high-contrast room-light-handleable elements of this invention are preferably utilized (exposed and processed) as sheet films. As such, the films preferably have low curl (i.e., less than about 40 ANSI curl units at 21°C and 15% relative humidity, using ANSI PH 1.29-1971, which calls for matching the curl of sample strips on a template of curves of varying radii to determine the radius of curvature and reporting the value of 100/R as the degree of curl where R is the radius of curvature in inches) and high dimensional stability (humidity coefficient, defined as % change in linear dimension divided by change in percent humidity over a 15-50% relative humidity range at 21°C, of less than about 0.0015).

[0054] In the photographic elements of this invention, an interlayer comprised of a hydrophilic colloid and a polymer latex can be interposed between the silver halide emulsion layer and the overcoat layer.

[0055] A primary purpose for the interlayer is to avoid, or at least reduce, "starry night" effect. This well-known effect can result from matting agent particles in an overcoat layer penetrating the silver halide emulsion layer. The image density in the area underlying a matting agent particle is diminished compared to other areas of the emulsion layer that have received equivalent exposure. These areas of decreased image density appear as small spots in the image. The resulting visual effect has been called the "starry night" effect due to the similarity in appearance to a starry night sky.

[0056] The interlayer is comprised of a mixture of a polymer latex and a hydrophilic colloid. The purpose of the polymer latex is to impart the necessary dimensional stability to the film and for this purpose, it is employed in an amount of from 0.2 to 1.5 parts per part by weight of the hydrophilic colloid. The hydrophilic colloid incorporated in the interlayer can be selected from among those described above as being useful in the emulsion layer and can be the same or different than the particular hydrophilic colloid used in the emulsion layer. Most preferably, the hydrophilic colloid in the interlayer is gelatin. The polymer latex incorporated in the interlayer can be selected from among those described above as being useful in the emulsion layer and can be the same or different than the polymer latex used in the emulsion layer. Most preferably, the polymer latex in the interlayer is poly(methylacrylate-co-2-acrylamido-2-methylpropane sulfonic acid).

[0057] The thickness of the interlayer is typically in the range of from 0.5 to 5 μm , preferably in the range of from 0.8 to 3.5 μm , and most preferably in the range of from 1.7 to 3 μm .

[0058] In a particularly preferred embodiment of the present invention, the silver halide grains are silver chloride grains, the mean grain size of the grains is about 0.1 μm , the dopant comprises ruthenium, the dopant is present in the grains in an amount of about 3×10^{-4} moles per silver mole, and 100 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume.

[0059] In the examples reported hereinbelow, a developer concentrate was formulated as follows and diluted at a ratio of one part of concentrate to four parts of water to produce a working strength developing solution with a pH of 10.4.

Sodium metabisulfite	145 g
45% Potassium hydroxide	178 g
Diethylenetriamine pentaacetic acid pentasodium salt (40% solution)	15 g
Sodium bromide	12 g

(continued)

Hydroquinone	65 g
1-Phenyl-4-hydroxymethyl-4-methyl-3-pyrazolidone	2.9 g
Benzotriazole	0.4 g
1-Phenyl-5-mercaptotetrazole	0.05 g
50% Sodium hydroxide	46 g
Boric acid	6.9 g
Diethylene glycol	120 g
47% Potassium Carbonate	120 g
Water to one liter	

[0060] The invention is further illustrated by the following examples of its practice.

Examples 1-4

[0061] High-contrast room-light-handleable black-and-white photographic elements in accordance with this invention were prepared using $K_2Ru(NO)Br_5$ as the doping agent. The elements comprised a poly(ethylene terephthalate) film support having, in order, on one side thereof a fine-grain high-chloride silver halide emulsion layer, an interlayer containing gelatin and a latex polymer, and an overcoat layer containing gelatin and a matting agent and having on the opposite side an antihalation layer containing gelatin, a latex polymer and antihalation dyes and a protective layer containing gelatin and a matting agent. The silver halide grains were one hundred percent chloride and had a mean grain size of 0.09 micrometers.

[0062] In the precipitation of the silver chloride emulsion, both the $AgNO_3$ and $NaCl$ solutions were added simultaneously at constant flow rates into a well-stirred reaction vessel containing gel/water at a pH of 3.0. The total run time of both reactants was 15 minutes and the reaction vessel temperature was maintained at 25°C. The emulsion precipitation was controlled at an mv value of +141. The emulsion was ultrafiltered at 40°C until a conductivity of 3.6 ms was reached. The final pH was 4.5 and the final mv value was +211.

[0063] In a control test, the dopant start time, that is the length of the time that elapsed from the start of the precipitation until addition of dopant began, was 30 seconds and the dopant interval time, that is the total time interval over which dopant was added, was 30 seconds. In Examples 1 to 4 either the dopant start time or the dopant interval time or both were varied from that used in the control test, as described in Table I below.

[0064] The photographic elements of the control test and of Examples 1 to 4 were exposed in an exposing device equipped with an iron-doped metal halide light source and processed using a developing solution as hereinabove described with a development time of 22 seconds at 35°C.

[0065] Intermittency and solarization were evaluated in accordance with the following test procedures:

Intermittency Test

[0066]

- (1) Place a 1.0 neutral density filter over the middle third of a 35-mm film strip.
- (2) Expose the strip with an iron-doped metal halide light source for 30 units.
- (3) Remove the neutral density filter and wait 2 minutes.
- (4) Cover the top third of the strip that received the first 30 unit exposure.
- (5) Give the strip another 30-unit exposure. The result is that the top third of the strip will have received a 30-unit exposure, the middle third will have received a 30-unit exposure attenuated with a 1.0 neutral density filter followed by a 30-unit exposure, and the bottom third will have received two 30-unit exposures.
- (6) Read the density of each area and record.

Solarization Test

[0067]

- (1) Using an exposure frame, expose each film strip at 94, 148, 236, 374, 598 and 944 units.
- (2) Read and record the densities.

[0068] The results obtained are summarized in Table I below.

Table I

<u>Example No.</u>	<u>Dopant Start Time (seconds)</u>	<u>Dopant Interval Time (seconds)</u>	<u>Wt. % of Dopant Within Outermost 90% of grain Volume</u>	<u>Solarization Test (D_{max})</u>	<u>Intermittency Test (D_{max})</u>
Control	30	30	0	3.7	3.4
1	30	100	40	4.9	4.2
2	30	170	65	5.3	4.7
3	170	30	100	5.2	5.6
4	170	100	100	5.4	5.8

[0069] Comparing Example 1 with the control test, it is seen that increasing the dopant interval time and thereby increasing the width of the dopant band provides an increased D_{max} in both the solarization test and the intermittency test. Comparing Example 2 with Example 1 indicates that a further increase in dopant interval time and consequently a further increase in the width of the band provides a further increase in D_{max} in both tests. Comparing Example 3 with the control test, it is seen that increasing the dopant start time and thereby shifting the location of the dopant band closer to the surface of the grain provides an increased D_{max} in both tests. Comparing Example 4 with Example 3 indicates that an increase in dopant interval time while maintaining dopant start time constant also provides an increased D_{max} in both tests.

[0070] In the control test, none of the dopant is located within the outermost 90 percent of the total grain volume. In each of Examples 1 to 4, more than 25 percent by weight of the dopant, namely 40, 65, 100 and 100 percent by weight for Examples 1 to 4, respectively, is located within the outermost 90 percent of the total grain volume. In Examples 3 and 4, which represent particularly preferred embodiments of the invention, all of the dopant is located within the outermost 90 percent of the total grain volume. As the data clearly demonstrate, controlling the location of the dopant

in the manner described herein effectively overcomes both solarization and intermittency problems.

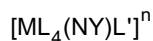
Claims

5
1. A high-contrast room-light-handleable black-and-white silver halide photographic element that is especially adapted for use in the field of graphic arts; the element comprising a support bearing a silver halide emulsion layer comprising fine-grain high-chloride radiation-sensitive silver halide grains exhibiting a face centered cubic crystal lattice structure internally containing a dopant comprised of a nitrosyl coordination ligand and a transition metal,

10
the element characterized wherein the dopant is present in the grains in an amount of from 5×10^{-6} to 3×10^{-4} mol/mol of silver,

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at least 25 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume to reduce the effects of solarization and intermittency on the emulsion and thereby enhance the maximum density of the element, and

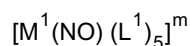
the dopant is represented by the formula:



wherein

25
M is ruthenium, rhenium or iridium;
L is bromide or cyanide;
L' is L;
Y is oxygen; and
n is zero, -1, -2, or -3.

30
2. The photographic element as claimed in claim 1, wherein the dopant is represented by the formula:



wherein

40
m is zero, -1, -2, or -3,
M¹ represents rhenium or ruthenium, and
L¹ represents bromide or cyanide ligand or a combination of these ligands with up to two aquo ligands.

- 45
3. The photographic element as claimed in either claim 1 or 2 wherein the transition metal is ruthenium.
4. The photographic element as claimed in any of claims 1 to 3 wherein bromide ligands are present with up to two aquo ligands.
5. The photographic element as claimed in any of claims 1 to 4 wherein the silver halide grains have a mean grain size of less than 0.4 μm, preferably less than 0.2 μm, and most preferably less than 0.1 μm.
- 50
6. The photographic element as claimed in any of claims 1 to 5 wherein the silver halide grains have a chloride content of at least 80 mole percent, preferably at least 90 mole percent, and most preferably 100 mole percent.
7. The photographic element as claimed in any of claims 1 to 6 wherein at least 50 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume.
- 55
8. The photographic element as claimed in any of claims 1 to 7 wherein 100 percent by weight of the total amount of the dopant within the grains is located within the outermost 90 percent of the total grain volume.

9. The photographic element as claimed in any of claims 1 to 8 wherein the dopant is $[\text{Ru}(\text{NO})\text{Br}_5]^{-2}$.
10. The photographic element as claimed in any of claims 1 to 9 wherein one more ammonium or alkali metal ions are associated with the dopant.

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Patentansprüche

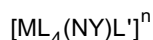
1. Unter Raumlicht handhabbares, speziell für grafische Anwendungen vorgesehenes, fotografisches Hochkontrast-Schwarzweiß-Silberhalogenidelement mit einem Träger, auf dem eine Silberhalogenid-Emulsionsschicht aufgebracht ist, welche feinkörnige, strahlungsempfindliche Silberhalogenidkörner mit hohem Chloridanteil umfasst, die eine flächenzentrierte kubische Kristallgitterstruktur aufweisen, die im Inneren eine Dotierung aus einem Nitrosylkoordinationsligand und ein Übergangsmetall enthalten.
- dadurch gekennzeichnet, dass die Dotierung in den Körnern in einer Menge von 5×10^{-6} bis 3×10^{-4} Mol/Mol von Silber vorliegt,

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dass sich mindestens 25 Gewichtsprozent der Gesamtmenge der Dotierung in den Körnern in den äußeren 90 Prozent des gesamten Kornvolumens befinden, um die Solarisations- und Intermittenzwirkung auf die Emulsion zu verringern und dadurch die Maximaldichte des Elements zu verbessern, und

dadurch gekennzeichnet, dass die Dotierung durch folgende Formel dargestellt wird:

20



25

wobei

M = Ruthenium, Rhenium oder Iridium;

L = Bromid oder Cyanid;

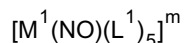
L' = Sauerstoff; und

n = null, -1, -2 oder -3.

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2. Fotografisches Element nach Anspruch 1, dadurch gekennzeichnet, dass die Dotierung durch folgende Formel dargestellt wird:

35



wobei

m = null, -1, -2 oder -3

M¹ stellt Rhenium oder Ruthenium dar; und

L¹ stellt Bromid- oder Cyanid-Ligand oder eine Kombination dieser Ligande mit bis zu zwei Aqualiganden dar.

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3. Fotografisches Element nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass das Übergangsmetall Ruthenium ist.

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4. Fotografisches Element nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass Bromidligande in bis zu zwei Aqualiganden vorkommen.

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5. Fotografisches Element nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Silberhalogenidkörner eine mittlere Größe von kleiner als $0,4 \mu\text{m}$ aufweisen, vorzugsweise von kleiner als $0,2 \mu\text{m}$ und am besten von kleiner als $0,1 \mu\text{m}$.

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6. Fotografisches Element nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass die Silberhalogenidkörner einen Chloridgehalt von mindestens 80 Molprozent aufweisen, vorzugsweise von mindestens 90 Molprozent und am besten von 100 Molprozent.

7. Fotografisches Element nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass sich mindestens 50

Gewichtsprozent der Gesamtmenge der Dotierung innerhalb der Körner in den äußeren 90 Prozent des gesamten Kornvolumens befinden.

- 5 8. Fotografisches Element nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, dass sich 100 Gewichtsprozent der Gesamtmenge der Dotierung innerhalb der Körner in den äußeren 90 Prozent des gesamten Kornvolumens befinden.
- 10 9. Fotografisches Element nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, dass die Dotierung $[\text{Ru}(\text{NO})\text{Br}_5]^{-2}$ ist.
10. Fotografisches Element nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, dass der Dotierung ein oder mehrere Ammonium- oder Alkalimetallionen zugeordnet sind.

15 **Revendications**

- 20 1. Élément photographique noir et blanc aux halogénures d'argent à contraste élevé, manipulable à la lumière ambiante, qui est spécialement adapté à une utilisation dans le domaine des arts graphiques ; cet élément photographique comprenant un support revêtu d'une couche d'émulsion aux halogénures d'argent comprenant des grains fins d'halogénures d'argent à haute teneur en chlorure sensibles aux rayonnements présentant une structure à réseau cristallin cubique à faces centrées contenant intérieurement un dopant comprenant un coordinat nitrosyle et un métal de transition,

25 l'élément photographique étant caractérisé en ce que le dopant est présent dans les grains en une quantité comprise entre 5×10^{-6} et 3×10^{-4} mole/mole d'argent, au moins 25 pourcent en poids de la quantité totale de dopant contenu dans les grains sont situés dans les 90 pourcent les plus à l'extérieur du volume total des grains pour réduire les effets de solarisation et d'intermittence sur l'émulsion et, par conséquent, améliorer la densité maximale de l'élément photographique, et le dopant est représenté par la formule :



35 dans laquelle

- M représente le ruthénium, le rhénium ou l'iridium ;
 L représente le bromure ou le cyanure ;
 L' est L ;
 Y représente l'oxygène ; et
 40 n est égal à zéro, -1, -2 ou -3.

2. Élément photographique selon la revendication 1, dans lequel le dopant est représenté par la formule :



dans laquelle

- m est égal à zéro, -1, -2 ou -3,
 50 M^1 représente un rhénium ou un ruthénium, et
 L^1 représente un coordinat bromure ou cyanure ou une combinaison de ces coordinats avec un maximum de deux coordinats aquo.

3. Élément photographique selon la revendication 1 ou 2, dans lequel le métal de transition est le ruthénium.
- 55 4. Élément photographique selon l'une quelconque des revendications 1 à 3, dans lequel les coordinats bromure sont présents avec un maximum de deux coordinats aquo.

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5. Élément photographique selon l'une quelconque des revendications 1 à 4, dans lequel les grains d'halogénures d'argent ont une granulométrie moyenne inférieure à 0,4 μm , de préférence inférieure à 0,2 μm , et idéalement inférieure à 0,1 μm .
- 5 6. Élément photographique selon l'une quelconque des revendications 1 à 5, dans lequel les grains d'halogénures d'argent ont une teneur en chlorure d'au moins 80 pourcent en moles, de préférence d'au moins 90 pourcent en moles, et idéalement de 100 pourcent en moles.
- 10 7. Élément photographique selon l'une quelconque des revendications 1 à 6, dans lequel au moins 50 pourcent en poids de la quantité totale de dopant contenu dans les grains sont situés dans les 90 pourcent les plus à l'extérieur du volume total des grains.
- 15 8. Élément photographique selon l'une quelconque des revendications 1 à 7, dans lequel 100 pourcent en poids de la quantité totale de dopant contenu dans les grains sont situés dans les 90 pourcent les plus à l'extérieur du volume total des grains.
- 20 9. Élément photographique selon l'une quelconque des revendications 1 à 8, dans lequel le dopant est $[\text{Ru}(\text{NO})\text{Br}_5]^{-2}$.
- 25 10. Élément photographique selon l'une quelconque des revendications 1 à 9, dans lequel un ou plusieurs ions ammonium ou ions de métal alcalin sont associés au dopant.
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