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(54) A photosensitive image-forming element containing tabular silver halide (iodo)bromide crystals which are internally modified with a metal ligand complex forming deep electron traps

Photoempfindliches bilderzeugendes Material, das tafelförmige Silber(iodo)bromidkristalle enthält, die mit einem Metall-Ligandenkomplex dotiert sind, der tiefe Elektronenfallen erzeugt

Matériau photosensible de formation d'image contenant des cristaux tabulaires à l'(iodo)bromure d'argent dopés avec un complexe métal-ligand, qui crée des pièges d'électrons profonds

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EP-A- 0 336 689
EP-A- 0 415 481
EP-A- 0 743 553
US-A- 5 462 849
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- **PATENT ABSTRACTS OF JAPAN vol. 018, no. 295 (P-1748), 6 June 1994 & JP 06 059365 A (KONICA CORP), 4 March 1994**
- **DATABASE WPI Section Ch, Week 9223 Derwent Publications Ltd., London, GB; Class E37, AN 92-189523 XP002069720 & JP 04 125629 A (KONICA CORP)**
- **U. HORNS AND W. PREETZ: "Darstellung und spektroskopische Charakterisierung von bindungsisomeren Halogenorhodanoosmaten(IV)" Z. ANORG. ALLG. CHEM., vol. 535, 1986, pages 195-207, XP002069718 LEIPZIG**

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a photosensitive silver halide emulsion and a photosensitive material containing said emulsion. More specifically the present invention is related to a tabular silver brom(iod)ide emulsion with enhanced image contrast.

BACKGROUND OF THE INVENTION

[0002] A silver halide material used for industrial applications needs a very high flexibility in its practical properties for use, like for instance the light temperature range for exposure, the range of development times in which an optimal image quality can be realized, etc.. On the other hand it is also necessary to have the disposal of means for the production of tailor-made silver halide materials for special applications which need for instance a well-defined gradation or sensitivity, etc.. One of the means increasingly used in the art, is the introduction of a deep electron trap in the silver halide crystal which can be arranged by doping with certain metal ligand complexes. Such an electron trap is called deep if it easily holds a captured electron. It can be energetically defined in the energy diagram if it fulfills the following two conditions: the LUMO (lowest unoccupied molecular orbital) of the incorporated molecular entity (related complex) should be situated at least 0.5 eV below the conduction band while the trapping lifetime should be longer than 0.2 s (R.S.Eachus, M.T.Olm in "Cryst.Latt.Def.and Amorph.Mat.", 1989(18), 297-313). The LUMO of the related complex thus has the ability to trap an electron from the conduction band (D.F.Shriver, P.W.Atkins, C.H.Langford in "Inorganic Chemistry"- Oxford Univ.Press (1990), Oxford-Melbourne-Tokyo).

[0003] A general property of a deep electron trapping agent (here further called 'DETA') is that it always creates loss in sensitivity which is inherent in this created lattice defect.

[0004] The DETA lowers the efficiency of the latent image formation process at the surface of the crystal by capturing a photo electron. Because the amount of these molecules is equally distributed over the solid silver halide the larger and intrinsically most sensitive emulsion grains will contain the most DETA-molecules (compared with the smaller less sensitive emulsion grains). These intrinsically most sensitive emulsion grains are therefore desensitized to a larger extent than the smaller and intrinsically less sensitive grains. This results in an overall desensitization and an increase of the overall gradation which can be most markedly seen in the so-called 'toe' of the sensitimetric curve, wherefrom the terminolgy 'toe-gradation' has been derived.

[0005] Specific examples are for instance $RuCl_5(NO)^{2-}$ and $OsCl_5(NO)^{2-}$ as described in EP-A 0 336 427 or the CO-ligand complexes as decribed in EP-A 0 415 481. These complexes give a very effective electron capturing defect in a silver halide crystal but the complex stability may be limited, especially when they are introduced in an aqueous medium at very high pAg-values and/or at high temperatures. Besides these aspects the availability of the said complexes is also limited because of the difficulty in synthesis and purification and, as a consequence thereof, of the high cost price.

[0006] Other examples of these complexes providing electron traps can be found in EP-A 0 606 895 and in US-A's 4,835,093; 5,348,850 and 5,616,446. In the US-A 5,616,446 e.g. an ultra hard image, even at low developing pH, and a wide dot tone reproduction region has been envisaged, which has been effectively realized therein by doping preferred cubic crystals rich in silver chloride with a rhodium, a ruthenium, an osmium and/or a renium compound in the core of the cubic grain emulsion as exemplified therein. Ligands set forth therein, differing from pure halides as (CN), (NO), (CO) and $(NH_3)$are (SCN), (SecN) and (TeCN), which have also been mentioned as ligands for the same metal atoms as in JP-A's 04-125629 and 06-059365_wherein high sensitivity, low fog and good reciprocity and latent image storage stability are envisaged respectively.

[0007] Another well-known metal ligand complex that can be used as a DETA in silver halide crystals is the $RhCl_6^{3-}$-complex in aqueous solutions which is especially active in a matrix rich in silver chlorobromide as has been demonstrated in EP-A 0 557 616 and in JP-A 6,035,093 and which is cheaper than the other complexes. However disadvantages related therewith are the formation of a chloro-aquo complex which is less active as a DETA, the activity decrease in a bromide or bromoiodide matrix and the impracticability in a silver chloride matrix.

[0008] Therefore it is highly desired to make silver halide materials which are doped with a new type of complex which acts as a DETA and which avoids all the problems and disadvantages as mentioned hereinbefore. Particularly desired is a metal halide complex producing a DETA that is new, stable in aqueous solutions, applicable in all types of silver halide matrices and easy to make with a low cost if compared with other DETA-producing complexes, moreover acting with a higher efficiency if compared with the $RhCl_6^{3-}$-complex representing the present state of the art.

OBJECTS OF THE INVENTION

[0009] It is therefore a first object of the present invention to provide a photosensitive material containing a silver halide emulsion with improved sensitometric properties.

[0010] It is a further object of the present invention to provide a photosensitive silver halide emulsion containing a DETA providing the formation of deep and permanent electron traps.

[0011] A still further object of the present invention is to provide a DETA as a dopant for photosensitive silver halide emulsions which can easily be prepared with relative low costs.

[0012] It is another object to provide a method to introduce a DETA having a constant composition.

[0013] Further objects and advantages of the present invention will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

[0014] The above mentioned objects are realized by providing a photosensitive image-forming element comprising on a support at least one photosensitive layer containing tabular silver brom(iod)ide crystals which are internally doped with a transition metal complex (more preferably a metal halide chalcogenic cyanate complex, further called a 'MHCC'-complex) thereby forming a deep and permanent electron trap, wherein said transition metal complex satisfies the following general formula

$$(1)\text{: } \mathrm{RHCl_{6-n}(H_2O)_{n1}(L)_{n2}m\text{-}} \qquad (1)$$

Wherein L represents a ligand having the formula $YCN^{(-)}$ or $NCY^{(-)}$, wherein Y represents S, Se or Te; n,n1 and n2 equal integers fulfilling the following equations: $1 \leq n < 6$ and $n = n1 + n2$, with $n2 \geq 1$; m equals an integer having a value of 1, 2 or 3; and wherein the metal complex satisfying formula (1) is situated in an inner portion of the silver halide crystals which contains not more than 50 mole % of the silver present in each crystal.

[0015] Preferred embodiments of the invention are disclosed in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The precipitation of a photosensitive silver halide emulsion is conducted in an aqueous dispersing medium including, at least during grain growth, a peptizer wherein silver ions and halide ions are brought together. Grain structure and properties can be selected by control of several parameters like precipitation temperature, pH and relative proportion of the silver and halide ions in the dispersing medium. In order to avoid fog formation the precipitation is commonly conducted on the halide side of the equivalence point which is defined as "the point at which the silver and halide ion activity is equal".

[0017] The silver halide emulsions of the current invention are prepared in the presence of compounds which can be occluded in the crystal structure. Such a compound (also called dopant) is replacing an appropiate amount of silver and halide ions in the silver halide lattice. The dopant can be distinguished from the metal-complex introduced in the emulsion as an additive by EPR-or ENDOR-techniques. The EPR-technique and sample preparation has been described in US-A 5,457,021 by Olm et al and by H.Vercammen, T.Ceulemans, D.Schoenmakers, P.Moens and D. Vandenbroucke in Proc. ICS&T of 49th Ann.Conf., p.54 (19-24 may,1996; Minneapolis). The description of the ENDOR-technique is given in the same Proc.Ann.Conf., p.56 by P.Moens, H.Vercammen, D.Vandenbroucke, F.Callens and D. Schoenmakers.

[0018] These so-called dopants are modifying the crystal structure and are further influencing the properties of the crystal. A lot of parameters like sensitivity, gradation, pressure sensitivity, high or low intensity reciprocity failure (LIRF), stability, dye desensitization, and several other sensitometric aspects of a photosensitive silver halide emulsion can be modified by selection of the dopant, including its concentration, its valency and its location in the crystal in case of incorporation of the single metal ion. When coordination complexes or even oligomeric coordination complexes are used the different ligands bound at the central metal ion can be occluded in the crystal lattice too and can in this way influence the photographic properties of the silver halide material as well (see Research Disclosure No. 38957 (1996) pag 591, section I-D). The dopant utilized in accordance with the present invention is a rhodium complex be defined by the general formula (1) as described hereinbefore and which is applied as a deep electron trapping agent or DETA.

[0019] The complex satisfying formula (1) contains at least one chalcogenic cyanate complex and differs from the other known chalcogenic cyanate complexes in different ways. There are for instance SCN- or NCS-containing complexes described (as in EP-A 0 336 425, EP-A 0 606 895, US-A 5,278,041 and US-A 5,609,997) which are used in silver halide materials as SET (shallow electron trap) and which cannot be applied for sensitivity decrease or gradation increase. In EP-A 0 336 427, EP-A 0 415 481 and US-A 4,981,781 other DET-producing complexes containing a NCS- or SCN-ligand are known and described but these do not contain halogen-ligands.

[0020] The metal halide complexes which are used for the present invention in order to create deep electron traps thus satisfy the following formula (1):

$$RhCl_{6-n}(H_2O)_{n1}(L)_{n2}m- \qquad (1)$$

wherein

n1, n2, m, and n represent integers having following values: $1 \leq n < 6$ and $n = n1 + n2$, with $n2 \geq 1$; m = 1, 2 or 3.

[0021] The ligand L in formula (1) is a chalcogenic cyanate group represented by YCN or NCY wherein Y represents a chalcogene atom selected from the group consisting of S, Se and Te.

[0022] In formula (1) it is further important that n equals an integer having a value from 1 up to less than 6, while m equals a value of 1, 2 or 3. A survey of possible structures for complex ions of Rh has been summarized in the Table 1 hereinafter,

Table 1

$RhCl_5(SCN)^{3-}$	$RhCl_5(SeCN)^{3-}$	$RhCl_5(TeCN)^{3-}$
$RhCl_5(NCS)^{3-}$	$RhCl_5(NCSe)^{3-}$	$RhCl_5(NCTe)^{3-}$
$RhCl_4(H_2O)(SCN)^{2-}$	$RhCl_4(H_2O)(SeCN)^{2-}$	$RhCl_4(H_2O)(TeCN)^{2-}$
$RhCl_4(H_2O)(NCS)^{2-}$	$RhCl_4(H_2O)(NCSe)^{2-}$	$RhCl_4(H_2O)\ (NCTe)^{2-}$
$RhCl_4(SCN)_2{}^{3-}$	$RhCl_4(SeCN)_2{}^{3-}$	$RhCl_4(TeCN)_2{}^{3-}$
$RhCl_4(NCS)_2{}^{3-}$	$RhCl_4(NCSe)_2{}^{3-}$	$RhCl_4(NCTe)_2{}^{3-}$
$RhCl_4(H_2O)_2(SCN)^{1-}$	$RhCl_4(H_2O)_2(SeCN)^{1-}$	$RhCl_4(H_2O)_2(TeCN)^{1-}$
$RhCl_4(H_2O)_2(NCS)^{1-}$	$RhCl_4(H_2O)_2(NCSe)^{1-}$	$RhCl_4(H_2O)_2(NCTe)^{1-}$

[0023] The complexes of the present invention satisfying formula (1) and which are used as deep electron trapping agents (DETA), can be prepared in different ways as described for instance for the CNS- or SCN-ligand complexes in 'Gmelins Handbuch der Anorganische Chemie' (Verlag Chemie,Germany), Vol.64(1955), p.70,71 and in US 3,507,928 (Rh-complexes).

[0024] For the preparation of the Rh-complexes used as dopants for tabular silver brom(iod)ide crystals in photosensitive layers in a photosensitive image-forming element of the present invention, said Rh-complexes being represented by formula (1), the following procedure was executed as described hereinafter for the $RhCl_6{}^{3(-)}$-complex with a SCN^- or a NCS^- -ligand. In the case of a SCN^- -complex the $RhCl_6{}^{3(-)}$-complex should be solved first in a concentrated aqueous $SCN^{(-)}$-solution which is kept at room temperature during a well-defined time in the range from 4 up to 24 hours, in order to form as a complex:

$$RhCl_6{}^{3-} + n1\ H_2O + n2\ SCN^- \leftrightarrow RhCl_{6-n}(H_2O)_{n1}(SCN)_{n2}{}^{[3-(6-n)-n2]}$$

and as n-n2=n1

$$RhCl_6{}^{3-} + n1\ H_2O + n2\ SCN^- \leftrightarrow RhCl_{6-n}(H_2O)_{n1}(SCN)_{n2}{}^{[-3+n1]}$$

wherein the index [-3+n1] equals as a value -m.

[0025] It is evident that a mixture of SCN-complexes is formed where n may have a value of from n=1 up to lower than 6. Therefore this reaction is spectrophotometrically followed until a certain absorption level is reached in order to provide introduction of the same mixture of complexes. The said mixture of complexes is the result of an exchange between the Cl- and the SCN-ligand which forms a more strongly bond with the metal atom(s) of the mixture of complexes and which is therefore also more stable. The amount of dopant which can effectively be incorporated in the emulsion grains in order to get the desired effect as described in the present invention should be situated in the range between 10^{-10} and 10^{-2} mole per mole of silver halide, preferably in the range between 10^{-9} and 10^{-4} mole per mole of silver halide and even more preferrably between 10^{-8} and 5.10^{-6} mole per mole of silver halide.

[0026] Introducing one or a mixture of at least two dopant(s) in the silver halide emulsion normally tends to increase the gradation of the image-forming element comprising the said emulsion after subsequent illumination and processing. Although being frequently accompanied by a decrease in photographic sensitivity this characteristic is used advantageously in photosensitive image-forming elements for roomlight or daylight operations. As has already been mentioned hereinbefore the location of the dopant may play a dominant role in fine-tuning the sensitometric characteristics of the material comprising emulsion grains containing one or more dopants. This is utilized advantageously in several applications where the dopant is non-uniformly distributed in the silver halide crystal.

[0027] For the present invention it is important that the complex(es) or dopant(s) according to formula (1) is(are) preferably concentrated in the inner portion of the silver halide crystals, wherein said inner portion is defined as the portion which contains less than 50 mole % of the silver present in each crystal, more preferably less than 25 mole % of the silver present in each crystal.

[0028] Introducing the dopants according to the general formula (1) in the photosensitive silver halide crystals coated in at least one photosensitive layer of a photosensitive image-forming element according to the present invention leads to an image-forming element with improved sensitometric characteristics with respect to gradation and sensitivity.

[0029] Dopants according to the formula (1) are essentially those which act as a deep and permanent electron trap in the silver halide crystal and which satisfy (as already taught hereinbefore) two conditions:

(a) the LUMO of the incorporated molecular entity should be at least 0.5 eV below the conduction band of the silver halide crystal, and
(b)the trapping life-time at room temperature should be longer than 0.2 seconds.

[0030] The doping procedure itself can normally be performed at any stage during the grain growth phase of the emulsion preparation where the reactants are added to the reaction vessel in the form of solutions of silver and halide salts or in the form of preformed silver halide nuclei or fine grains which easily dissolve in the precipitation medium. It is important to know that the dopants can also be added in an indirect way by addition of a dispersion containing very fine soluble silver halide grains or nuclei already comprising the dopant. Individual reactants for the formation of silver halide can be added through surface or subsurface delivery tubes by hydrostatic pressure or by an automatic delivery system for maintaining control of pH and/or pAg in the reaction vessel and of the rate of the reactant solutions introduced therein.

[0031] The reactant solutions or dispersions can be added at a constant rate or a constantly increasing or fluctuating rate in combination with stepwise delivery procedures as desired.

[0032] More details about possible ways of making a silver halide emulsion which can be principally used in practizising this invention are summarized in Research Disclosure No. 38957 (1996), p. 591-639, section I-C.

[0033] Special attention should be paid to the way in which the dopants are introduced during the grain growth process. Therefore the solution containing the dopants is preferentially introduced making use of a third jet, in a zone in the reactor wherein the compounds are rapidly incorporated in the growing microcrystals.

[0034] The advantage of the use of such a third jet is that a solvent can be used for the given dopant which is most suitable for the stability of that compound. Further the temperature of the dopant solution can be adjusted in order to maximize the stability too. The most stable conditions for the dopant solution are preferably tested by UV-VIS absorption. The third jet itself can be adjusted automatically or manually. The dopant can be added at a constant rate or at any rate profile as has e.g. been described in JP-A 03163438, wherein the dopant is occluded in two different concentrations in the silver halide grains of a direct positive emulsion, thereby having the highest dopant concentration closest to the grain centre. The said JP-Application describes a method to get a silver halide emulsion with improved gradation without paying attention to the sensitivity level, which, contrary thereto, is also one of the targets of the present invention.

[0035] The photographic emulsions prepared in this way for use in the image-forming element of the present invention contain tabular silver brom(iod)ide. Other silver salts which can be incorporated in a limited amount in the silver halide lattice are silver phosphate, silver thiocyanate, silver citrate and some other silver salts. Iodide ions can be coprecipitated with bromide ions in order to form a iodobromide with an iodide amount which depends on the saturation limit of iodide in the lattice with the given halide composition: this means up to a maximum amount of about 40 mole percent in silver iodobromide based on silver.

[0036] It should be noted in the context of the present invention that the activity of the complex(es) or dopant(s) satisfying formula (1) is almost not influenced by the brom(iod)ide composition of the silver brom(iod)ide crystals used.

[0037] The composition of the silver halide in the crystal volume can change in a continuous or in a discontinuous way. Emulsions containing crystals composed of various sections with different halide compositions are used for several differing photographic applications. Such a structure with a difference in halide composition between the center and the rest of the crystal (known as so-called "core-shell"-emulsion) or with more than two crystal parts differing in halide composition (called a "band"-emulsion) may occur. The changes in halide composition can be realized by direct precipitation or in an indirect way by conversion wherein fine silver halide grains of a certain predetermined halide composition are dissolved in the presence of the so-called host grains forming a "shell" or "band" on the given grain.

[0038] The crystals formed have a morphology which is tabular. In tabular crystals the aspect ratio (ratio of equivalent circular diameter to thickness) of the grains can vary from low (< 2) over "medium" or "intermediate" (from 2 up to 8) to "high" (> 8) where especially in the case of the ultrathin tabular crystals (from 0.05 up to 0.15 μm) high aspect ratios can be realized. The major faces of the tabular grains may have a {111} or a {100}-habitus, the structure of which is (respectively) stable or has to be stabilized (for instance by a "crystal habit modifying agent").

[0039] Besides the dopants which are deep electron traps as described by formula (1) other dopants can be added to the silver halide emulsion. These are optionally introduced, essentially because of their specific influence on the photographic characteristics. Different classes of dopants are known: dopants resulting in a non-permanent trapping behaviour or a shallow electron trap or SET (such as $IrCl_6^{3-}$ or $Ru(CN)_6^{2-}$, described in Research Disclosure No 36736 (1994), p. 657, or a recombination or hole trapping center. These dopants are essentially all those not obeying the conditions for creating a deep electron trap. Many examples of this category have already been described in the patent literature but cover different silver halide systems like e.g. those mentioned hereinbefore in WO 92/16876, EP-A 0 264 288, EP-A 0 552 650 and EP-A 0 752 614. It is a preferred option of the present invention that these non-permanent electron traps are present together with the DET-dopant(s) of formula (1).

[0040] After precipitation the emulsions can be coagulated and washed in order to remove any excess of aqueous soluble salts. These procedures are, together with different alternative methods like dia- or ultrafiltration and ion-exchange techniques, described in Research Disclosure No. 38957(1996), section III. The tabular silver brom(iod)ide emulsions coated in at least one photosensitive layer of the photosensitive image-forming element according to the present invention which are prepared in one of the ways described hereinbefore contain crystals which have a spherical equivalent diameter (SED) which is situated between 0.01 μm and 1.5 μm, more preferably between 0.01 μm and 1.0 μm and even more preferably between 0.01 μm and 0.9 μm. The spherical equivalent diameter (SED) of the crystal represents the diameter of the sphere which has the same volume as the average volume of the silver halide crystals of the said emulsion.

[0041] The emulsions can be surface-sensitive emulsions which form latent images primarily at the surface of the silver halide grains or they can be emulsions forming their latent-image primarily in the interior of the silver halide grain. Further emulsions. However direct-positive emulsions of the unfogged, latent image-forming type which are positive-working by development in the presence of a nucleating agent, and even pre-fogged direct-positive emulsions can be used in the present invention.

[0042] The silver halide emulsions can be surface-sensitized by chemical sensitization which can be done in many different ways, in presence of a chalcogen as sulfur, selenium or tellurium, in presence of a noble metal as e.g. gold or in combination with a chalcogen and noble metal. Sometimes it can be necessary to add a sulphur sensitizer in the form of a dispersion of solid particles as has been described in EP-A 0 752 614.

[0043] Reduction sensitization is another method of sensitizing a photosensitive silver halide emulsion which if desired can be combined with the chalcogen/noble metal-sensitization.

[0044] Reduction sensitization should especially be mentioned with respect to the present invention as a way of introducing hole traps in the silver brom(iod)ide crystals for use in the image-forming elements according to the present invention in order to optimize the efficiency of latent image formation. Reduction sensitization can be performed by decreasing pAg of the emulsion or by adding thereto reducing agents as e.g. tin compounds (see GB-Patent 789,823), amines, hydrazinederivatives, formamidine-sulphinic acids, silane compounds, ascorbic acid, reductic acid and the like. Care should however be taken in order to avoid generation of fog in an uncontrollable way.

[0045] It is clear that the incorporation of hole traps in silver halide can also be realized by incorporating special dopants like for instance $Cu^{(+)}$ and $Ni^{(2+)}$.

[0046] The presence of certain "modifying agents" as for instance spectral sensitizers which can optimize the chemical sensitization process are often used. A complete description of all the different possibilities with respect to this subject can be found in Research Disclosure No. 38957(1996), section IV.

[0047] In a next step the silver brom(iod)ide emulsions used in the image-forming elements according to the present invention are spectrally sensitized with dyes from different classes which include polymethine dyes comprising cyanines, merocyanines, tri-, tetra- and polynuclear cyanines and merocyanines, oxonols, hemioxonols, styryls, merostyryls and so on. Sometimes more than one spectral sensitizer may be used in the case that a larger part of the spectrum should be covered. Combinations of several spectral sensitizers are sometimes used to get supersensitization, which means that in a certain region of the spectrum the sensitization is greater than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Generally supersensitization can be attained by using selected combinations of spectral sensitizing dyes and other addenda such as stabilizers, development accelerators or inhibitors, brighteners, coating aids, and so on. A good description of all the possibilities in spectral sensitization which are important with respect to this invention can be found in Research Disclosure No. 38957(1996), section V. In the case that desensitizers should be used, as for instance in pre-fogged direct-positive or in daylight handling materials, various chemical compounds are proposed for practical use. Principally all these compounds which are used as desensitizers in silver halide materials and which are for instance summarized in EP-A 0 477 436 can be used in combination with the elements of the present invention.

[0048] The photographic elements comprising the said silver halide emulsions may include various compounds which should play a role of interest in the material itself or afterwards as e.g. in the processing, finishing or warehousing the photographic material.

[0049] These products can be stabilizers and anti-foggants (see RD No. 38957(1996), section VII), hardeners (RD No.38957(1996), section IIB), brighteners (RD No.38957(1996), section VI), light absorbers and scattering materials (RD No.38957(1996), section VIII), coating aids (RD No.38957(1996), section IXA), antistatic agents (RD No.38957 (1996) section IXC), matting agents (same RD No. 38957(1996), section IXD) and development modifiers (same RD, section XVIII). The silver brom(iod)ide material can also contain different types of couplers, which can be incorpated as described in the same RD, section X.

[0050] The photographic elements can be coated on a variety of supports as described in RD No. 38957(1996), section XV, and the references cited therein. The photographic elements may be exposed to actinic radiation, especially in the visible, near-ultraviolet and near-infrared region of the spectrum, in order to form a latent image (see RD No. 38957(1996) section XVI).

[0051] The latent-image formed can be processed in many different ways in order to form a visible image (same RD, section XIX).

[0052] So photothermographic materials are not excluded either. Processing to form a visible dye image for colour materials means contacting the element with a colour developing agent in order to reduce developable silver halide and to oxidize the colour developing agent which in turn normally reacts with the coupler to form a dye (RD. No. 38957 (1996), section XX).

[0053] The present invention can better be appreciated by referring to the following specific examples. They are intended to be illustrative and not exhaustive, about the requirements of the invention as described hereinbefore and as summarized in the claims nailing on to the essentials of this invention. The present invention, however, is not limited thereto.

EXAMPLES

Example 1 : Application to a tabular silver bromide emulsion.

[0054] For the preparation of this emulsion the following solutions were prepared:

- Solution C1:

KBr	1.47 g
Oxidized gelatin	7.5 g
H_2SO_4	8.35 g
demineralized water	3000 ml

- Solution C2:

$AgNO_3$	500 g
demineralized water	1500 ml

- Solution C3:

KBr	122.5 g
demineralized water	525 ml

- Solution C4:

KBr	224 g
KI	4.9 g
demineralized water	975 ml

- Solution C5:

gelatin	50 g

demineralized water 500 ml

- Solution C6:
  Polystyrene sulphonic
  acid (20 wt %) 40 ml
- Solution C7:

  KSCN 194.2g
  demineralized water in order to make a solution of 1 l.

- Solution Dot 5:

  $Na3[RhCl_6].12\ H_2O$ 0.088 g
  demineralized water 1000 ml
  pH = 2.25-2.50 adjusted with acetic acid.

- Solution Dot 6:

  KSCN 194.2 g
  Na3[RhC16]. 12 H2O 0.088 g
  demineralized water in order to make a solution of 1 l.

Note: Solution Dot 6 was allowed to stand 24-48 hours before precipitation.

The precipitation phase.

- *Comparative emulsion (1)*

[0055] The pH of the solution C1 was adjusted at a value of 1.8 with a sulphuric acid solution and pBr adjusted at 2.39 with Kbr. The solutions C2, C3 and C4 were kept at room temperature while solutions C1 and C5 were heated to 45° Celsius.

[0056] 7.35 ml of solution C2 and 12 ml of solution C3 were added to solution C1 in 9 seconds. After 2 minutes the temperature was elevated to 70 degrees in 25 minutes followed by the addition of solution C5 and adjusting of the pH at 6 with NaOH.

[0057] After waiting for 6 minutes the following steps are subsequently carried out:

- a first neutralization step with 41.25 ml of solution C3,
- a second neutralisation step with 7.5 ml of solution C2 during 1 minute, while solution C3 was added at a rate in order to keep the pAg constant at a value of 8.85,
- a first growth step adding solution C2 during 33.4 minutes at a constant growing rate (end rate of 23.1 ml/min is almost 3 times higher than the starting rate of 7.5 ml/min). Solution C3 was added in order to keep the pAg at 8.85,
- a third neutralization step with the addition of 7.5 ml of solution C2 during 7.5 minutes,
- a fourth neutralization step with the addition of solution C2 for 1 minute at a fixed rate and of solution C3 in such a way that the pAg was brought to 7.38,
- a second growing step wherein 911 ml of solution C2 was added at a constant growing rate from 7.5 ml/min to 36.9 ml/min during 41 minutes. Solution C3 was added in order to keep the pAg at 7.38.
- the addition of solution C6 in order to flocculate the emulsion followed by 3 washing cycles for desalting the emulsion.

[0058] After the washing procedure 112 g of gelatin and water was added to the precipitate in order to make a total weight of 3.5-3.75 kg. The pH was brought to 5.5 with citric acid and the pAg to 7.38 with a diluted $AgNO_3$ solution. The thus prepared silver bromoiodide emulsion has hexagonal tabular crystals in a numerical amount of about 95 % with a thickness of 210 nm and an average volumetric diameter d of 0.7 μm.

- *Comparative emulsion (2)*

[0059] Emulsion (2) was prepared in the same way, except that 1 ml of solution Dot 5, containing a Rhodium complex, was added to solution C1 at a constant rate using a third jet. The position of the dopant in the emulsion grains was expressed as a procentual amount of the crystal volume at the moment where the addition of the third jet was started and as a procentual amount of the crystal volume at the moment where the addition of the third jet was stopped. In this particular case it was situated between 20 and 25 %.

- *Inventive emulsion (3)*

[0060] Emulsion (3) was prepared in the same way, except that 1 ml of the solution Dot 6, containing a Rhodium complex, was added to solution C1 at a constant rate using a third jet. The position of the dopant in the emulsion grains was expressed as the procentual amount of the crystal volume at the moment where the addition of the third jet was started and the procentual amount of the crystal volume at the moment where the addition of the third jet was stopped. In this inventive emulsion it was situated between 20 and 25 % too.

- *Comparative emulsion (4)*

[0061] Emulsion (4) was prepared in the same way as in the inventive emulsion, except that 1 ml of the solution C7, containing only the KSCN salt, was added to solution C1 at a constant rate using a third jet.

[0062] The position of the salt in the emulsion grains was expressed as the procentual amount of the crystal volume at the moment where the addition of the third jet was started and the procentual amount of the crystal volume at the moment where the addition of the third jet was stopped. Also in this emulsion the KSCN salt was also situated between 20 and 25 %.

Chemical sensitization.

[0063] The tabular bromoiodide emulsions were ripened at a pAg and pH equal to 7.38 and 5.5 respectively with $8.9*10^{-3}$ mole per mole of silver of anhydro 5,5'-dichloro-3,3'-bis(n-sulphobutyl)-9-ethyl-oxacarbocyanine hydroxide as a spectral sensitizer, $1.4*10^{-3}$ mole of a potassium thiocyanate solution per mole of silver, $3.24*10^{-7}$ mole of a toluene sodium thiosulphonate solution per mole of silver, $1.5*10^{-5}$ mole of a sodium thiosulphate solution per mole of silver, $1.35*10^{-6}$ mole of a gold trichloride solution per mole of silver and $1.3 *10^{-4}$ mole of a mercaptotetrazole compound per mole of silver, at 55 °C for 200 minutes.

Coating procedure.

[0064] The emulsions were coated on a substrated PET base at 1.7 g gelatine/m2 and 5 g AgNO3/m2.

Exposure and processing.

[0065] The emulsions were image-wise exposed through a step-wedge originally using a 10^{-3} sec Xenon flash. The exposed photographic materials were developed in a surface developer at room temperature for 5 minutes and fixed for 5 minutes in a commercial fixer G333C (Trademark of AGFA) which was 1/3 diluted with demineralized water.

Evaluation of the results.

[0066] The fog levels for the materials were situated at about 0.07 for the ripened emulsions. The speed S measured was the logaritm of the energy of the illumination needed in order to obtain an optical density equal to 1 above fog level. The contrast G is measured around this point. All the values which are summarized in Table 2 are relative to the values of comparative emulsion (1) which is taken 100 % each time. For the sensitivity S a decrease of 50 % means a sensitivity loss with a factor of 2 while a decrease in gradation G is always proportional.

Table 2 : Sensitometric results.

	Speed S	Gradation G
Comparative (1)	100	100
Comparative (2)	89	105
Inventive (3)	98	129
Comparative (4)	*	*

* very low

[0067] The results from Table 2 demonstrate the strong increase of gradation for the emulsion for use in image-forming elements according to the present invention which is made by application of a dopant satisfying formula (1) of the present invention compared with the tabular emulsion which is doped with a $RhCl_6^{3-}$-complex as is normally used in the art for these applications.

Claims

1. A photosensitive image-forming element comprising on a support at least one photosensitive layer containing tabular silver brom(iod)ide crystals which are internally doped with a transition metal complex thereby forming a deep and permanent electron trap, wherein said transition metal complex satisfies the following general formula (1):

$$RHCl_{6-n}(H_2O)_{n1}\,(L)_{n2}^{\;m-}$$

wherein:

L represents a ligand having the formula $YCN^{(-)}$ or $NCY^{(-)}$, wherein Y represents S, Se or Te,
n,n1 and n2 equal integers fulfilling the following equations: $1 \leq n < 6$ and $n = n1 + n2$, with $n2 \geq 1$
m equals an integer having a value of 1, 2 or 3;

and wherein the metal complex satisfying formula (1) is situated in an inner portion of the silver halide crystals which contains not more than 50 mole % of the silver present in each crystal.

2. A photosensitive image-forming element according to claim 1, wherein the concentration of the dopant according to formula (1) is between 10^{-10} and 10^{-2} mole per mole of silver.

3. A photosensitive image-forming element according to claim 1 or 2, wherein the metal complex satisfying formula (1) is situated in an inner portion of the silver halide crystals which contains less than 25 mole % of the silver present in each crystal.

4. A photosensitive image-forming element according to any of claims 1 to 3, wherein the silver brom(iod)ide crystals contain one or more additional dopant(s) differing from the one described in formula (1) in that their electron trapping activity is non-permanent.

5. A photosensitive image-forming element according to any of claims 1 to 4, wherein the silver brom(iod)ide crystals are reduction sensitized.

6. A photosensitive image-forming element according to any of claims 1 to 5, wherein the silver brom(iod)ide crystals have a mean spherical equivalent diameter SED, wherein $0.01 \leq SED \leq 1.50$ µm.

7. A photo-sensitive image-forming element according to any of claims 1 to 6, wherein the complex satisfying formula (1) is situated in an inner portion of the tabular silver brom(iod)ide crystals after addition of 20% the total amount

of silver used.

8. A photo-sensitive image-forming element according to claim 7, wherein the complex satisfying formula (1) is situated in an inner portion of the tabular silver brom(iod)ide crystals before addition of 25 % of the total amount of silver used.

Patentansprüche

1. Ein strahlungsempfindliches Bilderzeugungselement, das auf einem Träger zumindest eine strahlungsempfindliche Schicht mit tafelförmigen Silberbromid(iodid)körnern enthält, die durch einen Übergangsmetallkomplex innendotiert sind, wodurch eine tiefe und permanente Elektronenfalle gebildet wird, wobei der Übergangsmetallkomplex der folgenden allgemeinen Formel (1) entspricht :

$$RhCl_{6-n}(H_2O)_{n1}(L)_{n2}^{m-} \qquad (1)$$

in der bedeuten :

L ein Ligand der Formel $YCN^{(-)}$ oder $NCY^{(-)}$, wobei Y S, Se oder Te bedeutet,
n, n1 und n2 ganze Zahlen, die den folgenden Gleichungen entsprechen : $1 \leq n < 6$ und $n = n1 + n2$, wobei $n2 \geq 1$,
m die ganze Zahl 1, 2 oder 3,

und wobei der Metallkomplex der Formel (1) in einem inneren Bereich der Silberhalogenidkristalle, der nicht mehr als 50 mol% des in jedem Kristall enthaltenen Silbers enthält, eingebettet ist.

2. Ein strahlungsempfindliches Bilderzeugungselement nach Anspruch 1, **dadurch gekennzeichnet, daß** das Verhältnis des Dotiermittels der Formel (1) zwischen 10^{-10} und 10^{-2} Mol pro Mol Silber liegt.

3. Ein strahlungsempfindliches Bilderzeugungselement nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** der Metallkomplex der Formel (1) in einem inneren Bereich der Silberhalogenidkristalle, der weniger als 25 mol-% des in jedem Kristall enthaltenen Silbers enthält, eingebettet ist.

4. Ein strahlungsempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet, daß** die Silberbromid(iodid)kristalle ein oder mehrere zusätzliche Dotiermittel, die sich durch ihre nicht-permanente elektroneneinfangende Aktivität zum Dotiermittel der Formel (1) unterscheiden, enthalten.

5. Ein strahlungsempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** die Silberbromid(iodid)kristalle durch Reduktion sensibilisiert sind.

6. Ein strahlungsempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, daß** die Silberbromid(iodid)kristalle einen Durchmesser eines sphärischen Äquivalenten (SED) zwischen 0,01 µm und 1,50 µm aufweisen.

7. Ein strahlungsempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet, daß** der Komplex der Formel (1) nach Zugabe von 20% der Gesamtmenge Silber in einem inneren Bereich der tafelförmigen Silberbromid(iodid)kristalle vorliegt.

8. Ein strahlungsempfindliches Bilderzeugungselement nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, daß** der Komplex der Formel (1) vor Zugabe von 25% der Gesamtmenge Silber in einem inneren Bereich der tafelförmigen Silberbromid(iodid)kristalle vorliegt.

Revendications

1. Elément photosensible de formation d'image comprenant, sur un support, au moins une couche photosensible

contenant des cristaux tabulaires de brom(iod)ure d'argent qui sont soumis à un dopage interne avec un complexe de métal transitoire, pour ainsi former un piège d'électrons profond et permanent, dans lequel ledit complexe de métal transitoire répond à la formule générale (1) ci-après :

$$RhCl_{6-n}(H_2O)_{n1}(L)_{n2}^{m-} \qquad (I)$$

dans laquelle

L représente un ligand répondant à la formule $YCN^{(-)}$ ou $NCX^{(-)}$ dans laquelle Y représente un atome de soufre, un atome de sélénium ou un atome de tellure,

n, n1 et n2 représentent des entiers répondant aux équations indiquées ci-après : $1 \leq n < 6$ et $n = n1 + n2$, $n2 \geq 1$,

m représente un entier possédant la valeur de 1, 2 ou 3 ;

et dans lequel le complexe métallique répondant à la formule (1) est situé dans une portion interne des cristaux d'halogénure d'argent, qui ne contient pas plus de 50 moles % de l'argent présent dans chaque cristal.

2. Elément photosensible de formation d'image selon la revendication 1, dans lequel la concentration du dopant répondant à la formule (1) se situe entre 10^{-10} et 10^{-2} mole par mole d'argent.

3. Elément photosensible de formation d'image selon la revendication 1 ou 2, dans lequel le complexe métallique répondant à la formule (1) est située dans une portion interne des cristaux d'halogénure d'argent qui contient moins de 25 moles % de l'argent présent dans chaque cristal.

4. Elément photosensible de formation d'image selon l'une quelconque des revendications 1 à 3, dans lequel les cristaux de brom(iod)ure d'argent contiennent un ou plusieurs dopants supplémentaires qui diffèrent de celui décrit dans la formule (1) par le fait que leur activité de capture d'électrons n'est pas permanente.

5. Elément photosensible de formation d'image selon l'une quelconque des revendications 1 à 4, dans lequel les cristaux de brom(iod)ure d'argent ont été sensibilisés par réduction.

6. Elément photosensible de formation d'image selon l'une quelconque des revendications 1 à 5, dans lequel les cristaux de brom(iod)ure d'argent possèdent un diamètre moyen équivalent à celui d'une sphère SED dans lequel $0{,}01 \leq SED \leq 1{,}50$ µm.

7. Elément photosensible de formation d'image selon l'une quelconque des revendications 1 à 6, dans lequel le complexe répondant à la formule (1) est situé dans une portion interne des cristaux tabulaires de brom(iod)ure d'argent après addition de 20 % de la quantité totale d'argent utilisée.

8. Elément photosensible de formation d'image selon la revendication 7, dans lequel le complexe répondant à la formule (1) est situé dans une portion interne des cristaux tabulaires de brom(iod)ure d'argent après addition de 25 % de la quantité totale d'argent utilisée.