(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 557 616 A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **92200343.9**

(22) Date of filing: **07.02.92**

(51) Int. Cl.5: **G03C 1/09**, G03C 8/06,
G03C 1/035

(43) Date of publication of application:
01.09.93 Bulletin 93/35

(84) Designated Contracting States:
BE DE FR GB

(71) Applicant: **AGFA-GEVAERT naamloze vennootschap**
Septestraat 27
B-2640 Mortsel(BE)

(72) Inventor: **The designation of the inventor has not yet been filed**

(54) A silver halide material suitable for use in a silver salt diffusion transfer process.

(57) The present invention provides an imaging element comprising on a support a photosensitive layer comprising silver halide grains having an average diameter between 0.35µm and 2µm and said silver halide grains being doped with a Group VIII metal salt characterized in that said silver halide grains are doped with said Group VIII metal salts in such an amount that equation (1) is satisfied:

$10^{-23}\text{m} < (\text{dop})^2.\text{r} < 10^{-20}\text{m}$ (1)

wherein dop represents the amount of the Group VIII metal salt added during the preparation of said silver halide grains (Mol/Mol of silver) and
r represents said average diameter.

EP 0 557 616 A1

1. Field of the invention.

The present invention relates to a silver halide emulsion for use in a silver salt diffusion transfer material. The present invention further relates to a method for obtaining an image using said material.

2. Background of the invention.

The principles of the silver halide diffusion transfer reversal process, herein called DTR-process, have been described e.g. in US-P 2,352,014 and in the book "Photographic Silver Halide Diffusion Process" by André Rott and Edith Weyde - The Focal Press - London and New York, (1972). In the DTR-process non-developed silver halide of an information-wise exposed photographic silver halide emulsion is transformed with a so-called silver halide solvent into soluble silver complex compounds which are allowed to diffuse into an image-receiving layer and are reduced therein with a developing agent, generally in the presence of physical development nuclei, to form a silver image having reversed image density values with respect to the silver image obtained in the exposed photographic material. The photosensitive material is a silver halide emulsion, usually of the negative type, i.e. producing an image having an optical density proportional to the amount of radiation received on exposure. At the exposed areas of the silver halide emulsion layer the silver halide is developed (chemical development) and thus cannot be dissolved any more to diffuse to the receiving layer. At the unexposed areas of the silver halide emulsion layer the silver halide is converted to a soluble silver complex salt and is transferred to the receiving layer, where it forms a silver image usually in the presence of physical development nuclei.

The DTR-process includes (a) a so-called "two-sheet" type where the silver halide emulsion layer and the image receiving layer are contained on separate supports and are brought in contact with each other at the time of diffusion transfer development to produce the silver image in the receiving sheet and (b) a so-called "mono-sheet" type where both the emulsion layer and the layer containing the physical development nuclei are contained on the same support.

A DTR-material has the advantage over other photographic material that higher maximum densities can be reached in the transferred image for moderate silver coverages, and that the images have normally better image qualities, such as sharpness and resolution. Nevertheless, the photographic speed is limited. A higher speed would imply a larger emulsion grain volume, but an increase in grain volume is restricted by the solvent reaction rate of the DTR-process. Another consequence of an increase in grain volume is a decrease in image quality of the transferred image i.e. a decrease in sharpness, contrast and resolution of the image.

The incorporation of certain Group VIII metal salts in silver halide emulsions is known to those skilled in the art to result in an enhancement of the contrast, together with an overall desensitization. Rhodium salts have found the greatest utility in this respect. Similar effects have been produced by incorporation of ruthenium, palladium, osmium and platinum as reported by J.W. Mitchell (Phot. Sci. Eng. 27 (2), p. 81, 1983). A DTR-material for application in the graphic art field generally comprises a photosensitive silver halide emulsion with an amount of a Group VIII metal containing compound larger than $2\ 10^{-7}$ mol pro mol of silver to improve contrast and sharpness of the image. However upon addition of group VIII metals the speed of the silver halide emulsion decreases.

3. Summary of the invention.

It is an object of the present invention to provide a DTR-imaging element having an improved speed and that can yield images of good quality especially of good contrast and sharpness.

It is a further object of the present invention to provide a method for obtaining an image of good contrast and sharpness according to the DTR process using a high speed DTR-imaging element.

Further objects of the present invention will become clear from the description hereinafter.

According to the present invention an imaging element is provided comprising on a support a photosensitive layer comprising silver halide grains having an average diameter between 0.35µm and 2µm and said silver halide grains being doped with a Group VIII metal salt characterized in that said silver halide grains are doped with said Group VIII metal salts in an amount not more than $2\ 10^{-7}$ mol pro mol of silver halide and so that equation (1) is satisfied:

$$10^{-23}\text{m} < (\text{dop})^2.\text{r} < 10^{-20}\text{m} \qquad (1)$$

wherein dop represents the amount of the Group VIII metal salt added during the preparation of said silver

halide grains (Mol/Mol silver) and
r represents said average diameter.

According to the present invention a method is provided for obtaining an image using said material in a DTR-process.

4. Detailed description of the invention.

In accordance with the present invention a DTR-material is provided containing a photosensitive silver halide emulsion layer and a layer containing physical development nuclei both layers on the same or on separate supports, said emulsion layer comprising silver halide grains having an average diameter "r" between 0.35 μm to 2.0 μm, and wherein during the preparation of said silver halide emulsion an amount "dop" (in mol/mol of silver halide) preferably between 2.0 10^{-9} to 2.0 10^{-7} mol pro mol of silver halide is added of a Group VIII metal containing compound so that:

$$10^{-23}\text{m} < (\text{dop})^2.\text{r} < 10^{-20}\text{m} \qquad (1)$$

More preferably the average diameter r of the silver halide grains is between 0.4μm and 2μm and most preferably between 0.5μm and 1.5μm. By the diameter of a silver halide grain is meant the diameter of a sphere with an equivalent volume as the corresponding silver halide grain. The average diameter r of the silver halide grains thus being the average of all these diameters.

The size distribution of the silver halide particles of the photosensitive silver halide emulsion layer to be used according to the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size. The average grain size and distribution can be measured by any of the well known techniques, such as described e.g. by T.H. James in "The Theory of the Photographic Process", fourth ed. , p.101, Macmillan Publishing Co. Inc., New York (1977), or by the method proposed by G. Moeller at the Int. Congress on Phot. Sci., Moskou (1970).

The photosensitive silver halide emulsion(s) can be prepared from soluble silver salts and soluble halides according to different methods as described e.g. by P. Glafkides in "Chimie et Physique Photografique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", The Focal Press, London (1966), and by V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966). The photosensitive silver halide emulsions used according to the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be prepared by any of the well known procedures e.g. single-jet emulsions or the double-jet emulsions such as Lippman emulsions, ammoniacal emulsions, thiocyanate- or thioether-ripened emulsions such as those described in US-A 2,222,264 - 3,320,069 and 3,271,157. The photosensitive silver halide emulsion(s) can also be prepared under Ostwald growth conditions, by continuously adding fine grains to the reaction vessel. The grains are grown in the absence or in the presence of any product having a site-directing activity.

The Group VIII metal containing compound is added preferably during the precipitation stage. The Group VIII metal containing compound may also be added at any time during the emulsion preparation, e.g. before or after any of the well known desalting stages of the emulsion, before or after adding any supplementary colloid binder, before or after any spectral or chemical sensitization or stabilization stage, etc.. The Group VIII metal is preferentially rhodium. However any other compound of metals of Group VIII or a mixture of compounds of metals of Group VIII, such as e.g. salts of cobalt, nickel, palladium, platinum and iridium may be used in accordance with the present invention. The amount of dopant "dop" in equation (1) is the total amount (in mol) of the Group VIII metal containing compound added pro mol silver at any stage of emulsion preparation. The total amount of metal containing compound "dop" can be added at once or in several steps, in one stage of the emulsion preparation, or during several stages of the emulsion preparation.

The photosensitive silver halide used in the present invention may comprise silver chloride, silver chlorobromide, silver chloroiodide, silver chlorobromoiodide and the like. To obtain a sufficiently high rate of solution of the silver halide emulsion grains in the DTR-processing step, the amount of bromide is between 0 and 40% more preferably between 0 and 30% and most preferably between 0 and 10% and the amount of iodide is between 0 and 5%, preferably between 0 and 2%, and most preferably between 0 and 0.2%.

The silver halide particles of the photographic emulsion may have a regular crystalline form such as cubic or octahedral form or they may have a transition form. The silver halide grains may also have an almost spherical form or they may have a tabular form (so-called T-grains), or may have composite crystal forms comprising a mixture of regular and irregular crystalline forms. The silver halide grains may have a multilayered structure having a core and at least one shell of different halide composition. Besides having a differently composed core and shell, the silver halide grains may comprise also different halide composition and metal dopants inbetween. Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming the silver halide emulsion used as a photosensitive layer in the DTR-material.

In addition to the photosensitive silver halide emulsion, a substantially light insensitive layer containing silver salt can be provided, having a speed of at least a factor 10 less than said photosensitive silver halide emulsion layer whereby said photosensitive silver halide is located between a image-receiving layer and the substantially light insensitive layer at the time of processing, as described in the application EP-A-91201577.3.

The photosensitive emulsion can be chemically sensitized e.g. by adding sulphur-containing compounds during the chemical ripening stage e.g. allyl isothiocyanate, allyl thiourea, and sodium thiosulphate. Also reducing agents e.g. the tin compounds described in BE-P 493,464 and 568,687, and polyamines such as diethylene triamine or derivatives of aminomethane-sulphonic acid can be used as chemical sensitizers. This method of chemical sensitization has been described in the article of R. Koslowsky, Z. Wiss. Photogr. Photophys. Photochem. 46, 65-72, (1951).

The photosensitive emulsion(s) of the photographic element of the present invention can be spectrally sensitized according to the spectral emission of the exposure source for which the photographic element is designed. Suitable sensitizing dyes for the visible spectral region include methin dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compouds", (1964), John Wiley & Sons. Dyes that can be used for this purpose include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particular valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes.

To enhance the sensitivity in the near infra-red region use can be made of so-called supersensitizers in combination with infra-red sensitizing dyes. Suitable supersensitizers are described in Research Disclosure Vol 289, May 1988, item 28952.

The spectral sensitizers can be added to the photosensitive emulsion(s) in the form of an aqueous solution, a solution in an organic solvent or in the form of a dispersion.

The silver halide emulsion(s) may contain the usual stabilizers e.g. homopolar or salt-like compounds of mercury with aromatic or heterocyclic rings such as mercaptotriazoles, simple mercury salts, sulphonium mercury double salts and other mercury compounds. Other suitable stabilizers are azaindenes, preferably tetra- or penta-azaindenes, especially those substituted with hydroxy or amino groups. Compounds of this kind have been described by Birr in Z. Wiss. Photogr. Photophys. Photochem. 47, 2-27, (1952). Other suitable stabilizers are i.a. heterocyclic mercapto compounds e.g. phenylmercaptotetrazole, quaternary benzothiazole derivatives, and benzotriazole. Preferred compounds are mercapto substituted pyrimidine derivatives as disclosed in US-P 3,692,527.

The silver halide emulsion layer comprises a hydrophillic colloid binder, which usually is gelatin. Mixtures of different gelatins with different viscosities can be used to adjust the rheological properties of the layer. But instead of or together with gelatin, use can be made of one or more other natural and/or synthetic hydrophillic colloids, e.g. albumin, casein, zein, polyvinyl alcohol, alginic acids or salts thereof, cellulose derivatives such as carboxymethyl cellulose, modified gelatin, e.g. phthaloyl gelatin etc.. The weight ratio of hydrophillic colloid binder to silver halide expressed as equivalent amount of silver nitrate to binder is e.g. in the range of 1:1 to 10:1.

The silver halide emulsion(s) may contain pH controlling ingredients. Preferably the emulsion layer is coated at a pH value below the isoelectric point of the gelatin to improve the stability characteristics of the coated layer. Other ingredients such as antifogging agents, development accelerators, wetting agents, and hardening agents for gelatin may be present. The silver halide emulsion layer may comprise light-screening dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes are described in i.a. US-P 4,092,168, US-P 4,311,787, DE-P 2,453,217, and GB-P 7,907,440.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-P 3,038,805 - 4,038,075 - 4,292,400.

More details about the composition, preparation and coating of silver halide emulsions can be found in e.g. Product Licensing Index, Vol. 92, December 1971, publication 9232, p. 107-109.

The image-receiving layer generally contains physical development nuclei. Suitable physical development nuclei for use in accordance with the present invention are e.g. colloidal silver, heavy metal sulphides e.g. silver sulphide, nickel sulphide, palladium sulphide, cobalt sulphide, zinc sulphide, silver nickel sulphide, etc.. The image-receiving layer containing the physical development nuclei may also contain a hydrophillic binder.

The photographic material of the present invention may contain additional hydrophillic layers, in water permeable relationship with the photosensitive emulsion layer, or the image-receiving layer. For example a hydrophillic layer may be applied as an outermost layer as a protecting or anti-stress layer. As an intermediate layer between the support and the silver halide emulsion layer(s), a hydrophillic layer can be provided, serving as a antihalation layer. This layer can contain the same light-absorbing dyes as described above for the emulsion layer ; as alternative finely divided carbon black can be used for the same antihalation purposes as described in US-P 2,327,828. On the other hand, in order to gain sensitivity, light reflecting pigments, e.g. titaniumdioxide can be present. Further this layer can contain hardening agents, matting agents, e.g. silica particles, and wetting agents.

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

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

The photographic element according to the present invention may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents or matting agents and plasticizers. Preferred spacing agents are SiO_2 particles having an average size between 0.8μm to 15μm. These spacing agents may be present in one or more layers comprised on the support(s) of the photographic material.

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

According to the present invention, the image-receiving layer and the light sensitive silver halide emulsion layer may be present on the same support, i.e. a so-called "mono-sheet" type DTR-material, as described in e.g. US-P 3,684,508. In this embodiment the silver halide emulsion grains are preferentially larger than 0.6 um, and contain an amount of a Group VIII metal containing compound in accordance to eq. (1).

According to the most preferred embodiment of the present invention the image-receiving layer and the light sensitive silver halide emulsion layer are contained on separate supports, brought in contact with each other at the time of diffusion transfer development, i.e. a so-called "two-sheet" type DTR-material. The material containing the image receiving layer is then called an image receiving material.

The support(s) of the photographical material and/or image receiving material used in accordance with the present invention can be any of the support materials customarily employed in the art. They include paper coated on one or both sides with an Alpha-olefin polymer, e.g. polyethylene, glass or film, e.g. cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethylene terephthalate film, etc.. Polyethylene terephthalate film coated with a subbing layer to improve the adhesion of the thereon deposited layers of the invention is preferred.

According to the method of the present invention for obtaining an image the photographic material is information-wise exposed and subsequently developed in an alkaline processing solution in the presence of (a) developing agent(s) and (a) silver halide solvent(s).

The photographic material of the present invention is exposed in an apparatus according to its particular application, e.g. a conventional process camera containing a conventional light source or a laser containing device.

Suitable developing agents for developing the exposed silver halide are e.g. hydroquinone-type and 1-phenyl-3-pyrazolidone-type developing agents as well as a p-monomethylaminophenol and derivatives thereof. Preferably used is a combination of a hydroquinone-type and 1-phenyl-3-pyrazolidone-type developing agent whereby the latter is preferably incorporated in one of the layers comprised on the support of the photographic material. A preferred class of 1-phenyl-3-pyrazolidone-type developing agents is disclosed in the European patent application number 90200458.9. Other type of developing agents suitable for use in accordance with the present invention are reductones e.g. ascorbic acid derivatives. Such type of developing agents are disclosed in the unpublished European patent application number 91200311.8. The developing agent or a mixture of developing agents can be present in an alkaline processing solution and/or in the photographic material. In case the developing agent or a mixture of developing agents is contained in the photographic material, the processing solution can be merely an aqueous alkaline solution that initiates and activates the development.

The pH of the alkaline processing solution is preferably between 10 and 13. The desired pH of the processing solution can be reached by incorporating alkaline substances in the processing solution. Suitable alkaline substances are inorganic alkali e.g. sodium hydroxide, potassium carbonate or aminoalcohols or mixtures thereof. Prefarably used alkanolamines are terriary alkanolamines e.g. those described in EP-A 397925, EP-A 397926, EP-A 398435 and US-P 4,632,896. A combination of alkanolamines having both a pK_a above or below 9 or a combination of alkanolamines whereof at least one has a pK_a above 9 and another having a pK_a of 9 or less may also be used as disclosed in the Japanese patent application laid open to the public numbers 73949/63, 73953/61, 169841/61, 212670/60, 73950/61, 73952/61, 102644/61, 226647/63, 229453/63, US-P 4,362,811, US-P 4,568,634 etc.. The concentration of these alkanolamines is preferably from 0.1 mol/l to 0.9 mol/l.

Preferably used silver halide solvents are water soluble thiosulphate compounds such as ammonium and sodium thiosulphate, or ammonium and alkali metal thiocyanates. Other useful silver halide solvents (or "complexing agents") are described in the book "The Theory of the Photographic Process" edited by T.H. James, 4th edition, p. 474-475 (1977), in particular sulphites and uracil. Further interesting silver halide complexing agents are cyclic imides, preferably combined with alkanolamines, as described in US-P 4,297,430 and US-P 4,355,090. 2-mercaptobenzoic acid derivatives are described as silver halide solvents in US-P 4,297,429, preferably combined with alkanolamines or with cyclic imides and alkanolamines.

The silver halide solvent(s) may be partly or completely present in the photographic material. When the silver halide solvent is incorporated in the photographic material it may be incorporated as a silver halide solvent precursor as disclosed in e.g. Japanese published unexamined patent applications no. 15247/59 and 271345/63, US-P 4,693,955 and US-P 3,685,991.

Developing of the information-wise exposed photographic material is preferably carried using a single processing liquid. However use can be made of two processing liquids whereby only the second liquid that is applied comprises a silver halide solvent.

According to the most preferred method of the present invention an imaging element comprising on a support a silver halide emulsion according to the present invention is information-wise exposed and subsequently developed in the presence of developing agent(s) and silver halide solvent(s) whilst in contact with an image receiving material comprising on a support a layer containing physical development nuclei.

Most of the image receiving materials also called DTR-positive materials now available on the market are composed of two or even three layers. Such materials normally contain on top of the nuclei containing layer a layer which itself contains no nuclei and otherwise has the same composition as the nuclei containing layer and mainly serves to ensure good contact between the negative and positive material during transfer. Moreover, after drying this layer provides a protective coating for the image receiving layer containing the silver image. It further prevents bronzing or plumming of the black image areas in preventing the protruding of silver from the image receiving layer in the form of a glossy silver mirror (ref. the above mentioned book p. 50).

According to the present invention the processing liquid and/or the image-receiving element preferably contains at least one image toning agent. In said case the image toning agent(s) may gradually transfer by diffusion from said image-receiving element into the processing liquid and keep therein the concentration of said agents almost steady.

A survey of suitable toning agents is given in the above mentioned book of André Rott and Edith Weyde, p. 61-65, preference being given to 1-phenyl-1H-tetrazole-5-thiol, also called 1-phenyl-5-mercapto-tetrazole, tautomeric structures and derivatives thereof such as 1-(2,3-dimethylphenyl)-5-mercapto-tetrazole, 1-(3,4-dimethylcyclohexyl)-5-mercapto-tetrazole, 1-(4-methylphenyl)-5-mercapto-tetrazole, 1-(3-chloro-4-methylphenyl)-5-mercapto-tetrazole, 1-(3,4-dichlorophenyl)-5-mercapto-tetrazole. Further particularly useful toning agents are of the class of thiohydantoins. Other particularly useful silver image toning agents are in the class of phenyl substituted mercapto-triazoles.

Still further toning agents suitable for use in accordance with the present invention are the toning agents described in the European patent applications 218752, 208346, 218753 and US-P-4683189.

According to a practical embodiment in the image-receiving element a hydrophilic colloid layer in waterpermeable relationship with the development nuclei containing layer or a back layer at the side of the support opposite to that carrying the image receiving layer contains at least part of the silver image toning agents. Such procedure results actually in automatic replenishment of toning agent in the processing liquid. The same applies at least partially for the replenishment of the developing agent(s) and silver halide complexing agent(s).

According to another embodiment at least a part of said silver image toning agents is present in the silver halide emulsion material to be developed. Such means that in a practical embodiment at least one of the image toning agents may be used in a hydrophilic waterpermeable colloid layer, e.g. antihalation layer at the side of the support opposite to the side coated with a silver halide emulsion layer or between the support and the silver halide emulsion layer. The coverage of said silver image toning agents in said antihalation layer is preferably in the range of 10 mg/m^2 to 100 mg/m^2.

The transfer behaviour of the complexed silver largely depends on the thickness of the image-receiving layer and the kind of binding agent or mixture of binding agents used in the nuclei containing layer. In order to obtain a sharp image with high spectral density the reduction of the silver salts diffusing into the image receiving layer must take place rapidly before lateral diffusion becomes substantial. An image-receiving material satisfying said purpose is described in US-4,859,566.

An image-receiving material of this type is very suitable for use in accordance with the present invention and contains a water-impermeable support coated with (1) an image-receiving layer according to the invention containing physical development nuclei dispersed in a waterpermeable binder and (2) a waterpermeable top layer free from development nuclei and containing a hydrophilic colloid, in such a way that :

(i) the total solids coverage of said two layers (1) and (2) is at most 2 g/m^2,

(ii) in layer (1) the coverage of the nuclei is in the range of 0.1 mg/m^2 to 10 mg/m^2, and the coverage of binder is in the range of 0.4 to 1.5 g/m^2, and

(iii) in said top layer (2) the coverage of hydrophilic colloid is in the range of 0.1 to 0.9 g/m^2.

The coating of said layers proceeds preferably with slide hopper coater or curtain coater known to those skilled in the art.

A white appearance of the image background even when a yellow stain should appear on storage is obtained by incorporation of optical brightening agents in the support, image-receiving layer and/or interlayer between the support and the image-receiving layer.

According to a particular embodiment the nuclei containing layer (1) is present on a nuclei-free underlying hydrophilic colloid undercoat layer or undercoat layer system having a coverage in the range of 0.1 to 1 g/m^2 of hydrophilic colloid, the total solids coverage of layers (1) and (2) together with the undercoat being at most 2 g/m^2.

The undercoat optionally incorporates substances that improve the image quality, e.g. incorporates a substance improving the image-tone or the whiteness of the image background. For example, the undercoat may contain a fluorescent substance, silver complexing agent(s) and/or development inhibitor releasing compounds known for improving image sharpness.

According to a special embodiment the image-receiving layer (1) is applied on an undercoat playing the role of a timing layer in association with an acidic layer serving for the neutralization of alkali of the image-receiving layer. By the timing layer the time before neutralization occurs is established, at least in part, by the time it takes for the alkaline processing composition to penetrate through the timing layer. Materials suitable for neutralizing layers and timing layers are disclosed in Research Disclosure July 1974, item 12331 and July 1975, item 13525.

In the image-receiving layer (1) and/or in said top layer (2) and/or in an undercoat gelatin is used preferably as hydrophilic colloid. In layer (1) gelatin is present preferably for at least 60 % by weight and is optionally used in conjunction with an other hydrophilic colloid, e.g. polyvinyl alcohol, cellulose derivatives, preferably carboxymethyl cellulose, dextran, gallactomannans, alginic acid derivatives, e.g. alginic acid sodium salt and/or watersoluble polyacrylamides. Said other hydrophilic colloid may be used also in the top layer for at most 10 % by weight and in the undercoat in an amount lower than the gelatin content.

The image-receiving layer and/or a hydrophilic colloid layer in water-permeable relationship therewith may comprise a silver halide developing agent and/or silver halide solvent, e.g. sodium thiosulphate in an amount of approximately 0.1 g to approximately 4 g per m^2.

The image-receiving layer or a hydrophilic colloid layer in water-permeable relationship therewith may comprise colloidal silica.

The image-receiving layer may contain as physical development accelerators, in operative contact with the developing nuclei, thioether compounds such as those described e.g. in DE-A-1,124,354; US-A-4,013,471; US-A-4,072,526; and in EP 26520.

When applying an optical brightening agent in the image-receiving material preference is given to an optical brightening agent that is inherently by its structure resistant to diffusion or is made resistant to diffusion by use in conjunction with another substance wherein it is dissolved or whereto it is adsorbed.

For example, to make an optical brightening agent resistant to diffusion one of the following techniques may be applied.

According to a first technique known from colour photography the optical brightening compound is substituted with a long chain aliphatic residue and ionomeric residue as is known in the synthesis of diffusion resistant colour couplers.

According to a second technique an optical brightening agent of the oleophilic type is incorporated in droplets of a water-immiscible solvent, so-called "oilformer", e.g. dibutylphthalate.

According to a third technique the optical brightening agent is used in conjunction with a polymeric hydrophilic colloid adsorber, a so-called trapping agent, e.g. poly-N-vinylpyrrolidinone as described e.g. in US-P 3,650,752, 3,666,470 and 3,860,427 and published European patent application 0 106 690.

According to a fourth technique latex compositions are used wherein latex particles are loaded, i.e. contain in dissolved and/or adsorbed state an optical brightening agent as described e.g. in German Offenlegungsschrift (DE-OS) 1,597,467 and in US-P 4,388,403.

The image-receiving layer and/or other hydrophilic colloid layer of an image-receiving material used in a DTR-process according to the present invention may have been hardened to some extent to achieve enhanced mechanical strength. Appropriate hardening agents for hardening the natural and/or synthetic hydrophilic colloid binding agents in the image-receiving layer include e.g. formaldehyde, glyoxal, mucochloric acid, and chrome alum. Other suitable hardening agents for hardening the hydrophilic colloid binding agents in the image-receiving layer are vinylsulphonyl hardeners, e.g. as described in Research Disclosure 22,507 of Jan. 1983.

According to a preferred embodiment hardening is effected by incorporating a hardener precursor in the image-receiving layer, the hardening of the hydrophilic colloid therein being triggered by the treatment with an alkaline processing liquid during processing.

In the process of the present invention the image-receiving material can be used in the form of roll film or sheet film or in the form of a filmpack e.g., for in-camera-processing.

The present invention is illustrated with the following examples without limiting it thereto. All parts are by weight unless otherwise specified.

EXAMPLE

Preparation of the photosensitive silver halide emulsions :

Solution 1	gelatin water	50 g 1000 ml
Solution 2	$AgNO_3$ water	500 g 1000 ml
Solution 3.1.	NaCl KBr $K_3RhCl_6.12H_2O$ water	167.0 g 6.3 g 115 µg 1000 ml
Solution 3.2.	NaCl KBr $K_3RhCl_6.12H_2O$ water	167.0 g 6.3 g 230 µg 1000 ml
Solution 3.3.	NaCl KBr $K_3RhCl_6.12H_2O$ water	167.0 g 6.3 g 346 µg 1000 ml
Solution 3.4.	NaCl KBr $K_3RhCl_6.12H_2O$ water	167.0 g 6.3 g 392 µg 1000 ml
Solution 3.5.	NaCl KBr $K_3RhCl_6.12H_2O$ water	167.0 g 6.3 g 461 µg 1000 ml

Solution 1 was heated to 60 °C and the solutions 2 and 3 were kept at room temperature. Solution 1 was brought to pH 4.0 with a sulphuric acid solution and to a pAg of 7.15 with a sodium chloride solution. Subsequently solution 2 was added at a constant rate, while the corresponding solution 3 was added at a rate so as to keep the pAg at 100mV. Solution 2 was further added at an accelerating rate, while solution 3 was added at a rate sufficient to keep the pAg constant. The resulting silver halide was precipitated by adding a polystyrene sulphonic acid. The precipitate was rinsed several times and redispersed by adding 200 g gelatin per 2.2 kg of the precipitate. The thus prepared silver halide emulsions containing 1.8 mol % silver bromide and 98.2 mol % silver chloride have homodisperse grain size distributions ; the average grain size "r" is given in table 1.

Table 1 : Emulsion specifications.

Emulsion number	Grain size (µm)	Var. (%)	Halide solution	mol Rh/mol Ag ($\times 10^{-7}$)	$dop^2.r$ ($\times 10^{-24}$)
1	0.30	12	3.4	2.05	12608
2	0.48	11	3.1	0.60	1745
3	0.48	13	3.2	1.21	7028
4	0.48	11	3.5	2.41	27879
5	0.67	10	3.1	0.60	2436
6	0.66	12	3.5	2.41	38333
7	0.84	12	3.3	1.81	27519
8	1.01	11	3.1	0.60	3672
9	1.01	11	3.5	1.21	14787

1.25 ml of a 3 molair solution of potassium iodide was added per 50 g silver expressed as $AgNO_3$. The silver halide emulsions were subsequently ripened with gold and thiosulphate for 3 hours at 50 °C, and stabilzed with triazaindolizine. The silver halide emulsions were spectrally sensitized with a green (ortho) sensitizer, and further stabilized with a sulphomercapto compound.

Preparation of the photographic materials

To a polyethylene terephthalate film support coated with a hydrophillic adhesion layer were coated, in the order given:

- a antihalation layer containing finely divided carbon black, developing agents such as hydroquinone (5.37 mmol/m^2) and 1-phenyl-3-pyrozolidone (2.01 mmol/m^2) and hardening agents.
- one of the photosensitive silver halide emulsions of table 1. The emulsion was coated at 2 g $AgNO_3/m^2$. The gelatin content was 2.62 g gelatin/m^2.
- a top layer containing a latex, wetting agents and hardening agents.

Preparation of the image receiving material

One side of a paper support having a weight of 110 g/m^2 and being coated at both sides with a polyethylene layer was coated at a dry coverage of 2 g/m^2 with an image-receiving layer containing silver-nickel sulphide nuclei and gelatin. This layer was applied by slide hopper coating so that the nuclei were in an undermost coating of 1.3 g gelatin per m^2 and a top layer was provided of 0.7 g of gelatin per m^2.

Composition of the processing liquid:

hydroxyethyl cellulose (g)	1.0
Ethylenediaminetetraacetic acid tetrasodium salt (g)	2.0
Na_2SO_3 (g)	45.0
$Na_2S_2O_3$ (g)	14.0
KBr (g)	0.5
1-Phenyl-5-mercapto-tetrazole (g)	0.1
1-(3,4-Dichlorophenyl)-1H-tetrazole-5-thiol (g)	0.02
N-methyl-ethanolamine (ml)	45.0
N-methyl-diethanolamine (ml)	30.0
Water up to	1 l

The photographic materials were image-wise exposed through an original for 10 seconds with a halogen light source. The exposed photographic materials were pre-moistened with the above described processing liquid, the contact time with said liquid being 6 seconds before being pressed together with an image-receiving material as defined above. The transfer processor employed was a COPYPROOF (registered trade name of AGFA-GEVAERT N.V.) type CP 380. The transfer contact time was 15 seconds for the paper type image receiving materials and 60 seconds for the resin film type image receiving materials.

The minimum and maximum reflection density, the speed and the gamma value (maximum gradient of the straight line portion of the sensitometric curve) were measured. The results are shown in table 2. The relative speed is the percentage of the energy of the illumination needed to obtain an optical density exceeding 1 above fog relative to the first emulsion. A lower number thus indicates an increased speed.

Table 2

Sensitometric data.					
Emulsion number	D_{min}	D_{max}	rel. speed	gamma	
1	.10	2.02	100	8.7	comparitive
2	.10	1.97	39	9.6	
3	.10	2.00	83	12.3	
4	.10	1.94	357	19.6	comparitive
5	.10	1.98	81	12.1	
6	.11	2.00	1111	17.1	comparitive
7	.11	2.00	667	17.5	comparitive
8	.11	1.98	95	13.1	
9	.10	1.97	227	17.1	comparitive

As can be seen from table 2 the speed for the samples according to the invention is increased while the contrast and sharpness as revealed by the values of D_{min}, D_{max} and gamma are maintained or improved.

Claims

1. An imaging element comprising on a support a photosensitive layer comprising silver halide grains having an average diameter between 0.35µm and 2µm, and said silver halide grains being doped with a Group VIII metal salt characterized in that said silver halide grains are doped with said Group VIII metal salts in such an amount that equation (1) is satisfied:

   $10^{-23}m < (dop)^2.r < 10^{-20}m$ (1)

   wherein dop represents the amount of the Group VIII metal salt added during the preparation of said silver halide grains (Mol/Mol of silver) and r represents said average diameter.

2. An imaging element according to claim 1 wherein said photosensitive silver halide emulsion is a silver chlorobromide emulsion containing an amount of bromide between 0 and 40%.

3. An imaging element according to claim 1 wherein said photosensitive silver halide emulsion is doped with a mixture of Group VIII metal containing compounds.

4. An imaging element according to any of the preceding claims wherein said group VIII metal compound is a rhodium compound.

5. An imaging element according to any of the preceding claims wherein said diameter r is between 0.5µm and 1.5µm.

6. An imaging element according to any of the preceding claims further comprising an image-receiving layer containing physical development nuclei.

7. A method for obtaining an image according to the silver salt diffusion transfer process, comprising the steps of information-wise exposing an imaging element as defined in any of claims 1 to 5 and subsequently developing said information-wise exposed imaging element in the presence of developing agent(s) and silver halide solvent(s) whilst in contact with a receiving element comprising on a support a layer containing physical development nuclei.

8. A method for obtaining an image according to the silver salt diffusion transfer process, comprising the steps of information-wise exposing an imaging element as defined in claim 6 and subsequently developing said information-wise exposed imaging element in the presence of developing agent(s) and silver halide solvent(s).

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 20 0343

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-1 535 016 (ILFORD LTD.) * column 2, line 22 - line 31; claims * ---	1-4	G03C1/09 G03C8/06 G03C1/035
A	DATABASE WPIL Week 8433, Derwent Publications Ltd., London, GB; AN 84-204147 & JP-A-59 116 659 (KONISHIROKU PHOTO KK) 5 July 1984 * abstract * ---	1-8	
A	EP-A-0 423 399 (AGFA-GEVAERT) * claims * ---	1-8	
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 109 (P-355)(1832) 14 May 1985 & JP-A-59 231 530 (KONISHIROKU SHASHIN KOGYO) 26 December 1984 * abstract * ---	1,5	
A	FR-A-2 132 095 (POLAROID CORP.) * page 4, lines 11-19; page 6, lines 30-38 * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	EP-A-0 350 046 (FUJI PHOTO FILM COMPANY) * page 44; table 1 * -----	1	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	15 OCTOBER 1992	STOCK H.

CATEGORY OF CITED DOCUMENTS

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

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

& : member of the same patent family, corresponding document