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

(72)

Inventor: **Vermeulen, Leon, c/o Agfa-Gevaert  
N.V.  
DIE 3800, Septestraat 27,  
B-2640 Mortsel, (BE)**  
Inventor: **De Smedt, Willy, c/o Agfa-Gevaert  
N.V.  
DIE 3800, Septestraat 27,  
B-2640 Mortsel, (BE)**  
Inventor: **Pauwels, Robert, c/o Agfa-Gevaert  
N.V.  
DIE 3800, Septestraat 27,  
B-2640 Mortsel, (BE)**

(54)

**An imaging element for use in a silver salt diffusion transfer process.**

(57)

The present invention discloses an imaging element comprising on a support (i) a photosensitive layer containing an amount of silver halide expressed as AgNO<sub>3</sub> between 0.6g/m<sup>2</sup> and 2.0g/m<sup>2</sup> and hydrophilic colloid in a total amount between 0.5g/m<sup>2</sup> and 2.0g/m<sup>2</sup>, (ii) an antihalation substance and (iii) TiO<sub>2</sub> provided under the photosensitive layer of the imaging element when viewed from its photosensitive side. There is further disclosed a method for obtaining an image according to the silver salt diffusion transfer process with said imaging element. The imaging element according to the present invention is less susceptible to exhausture of the processing liquid.

**EP 0 611 991 A1**

## 1. Field of the invention.

The present invention relates to an imaging element for use in a silver salt diffusion transfer process and to a method for obtaining images therewith.

## 2. Background of the invention.

The principle of the silver complex diffusion transfer process (hereinafter referred to as DTR process) is well known from the description in U.S. Pat. NO. 2,352,014 and in the book "Photographic Silver Halide Diffusion Processes" by André Rott and Edith Weyde - The Focal Press - London and New York, (1972).

In the DTR process, the silver complex is imagewise transferred by diffusion from a silver halide emulsion layer to an image receptive layer and transformed therein into a silver image generally in the presence of physical development nuclei. For this purpose, the imagewise exposed silver halide emulsion layer is arranged so as to be in contact with or is brought into contact with the image receptive layer in the presence of a developing agent and a solvent for the silver halide, thereby to convert the unexposed silver halide into a soluble silver complex. In the exposed areas of the silver halide emulsion layer, the silver halide is developed into silver which is insoluble and, hence, cannot diffuse. In the unexposed areas of the silver halide emulsion layer, the silver halide is converted into a soluble silver complex and is transferred to an image receptive layer wherein the silver complex forms a silver image generally in the presence of development nuclei.

The DTR process can be utilized in a wide field such as reproduction of documents, making of printing plates, preparation of black copies, and instant photography.

Particularly in reproducing documents or preparing black copies, an imaging element having a silver halide emulsion layer is brought into close contact with a positive material having an image receptive layer in a DTR processing solution generally containing a silver-complexing agent, thereby to form a silver image in the receptive layer of the positive material. The silver image in these cases is required to be pure black or bluish black in color and sufficiently high in density. It is also important that the silver image be high in contrast and sharpness, excellent in image reproducibility, and preferably high in transfer speed. In addition, these properties of the positive material should not be greatly dependent upon the processing conditions such as, for example, processing time and temperature.

In order to produce less waste it is desirable to increase the quantity of photographic material that can be processed per liter of processing liquid. Attempts have been made to improve the running characteristics of a processing liquid by adopting the composition thereof as described in e.g. EP-A-397925, EP-A-397926, EP-A-397927, EP-A-398435 and US-P-4.632.896.

On the other hand one could also adopt the constitution of the photographic material. For example in US-P-5.041.354 it has been described that the running characteristics of a processing liquid can be improved by setting the total amount of hydrophilic colloid on the photosensitive side between 6 and 8g/m<sup>2</sup> while keeping the swelling ratio between 3.5:1 and 5.5:1. It is also exemplified in this disclosure that the further reduction of the total amount of hydrophilic colloid below 6g/m<sup>2</sup> results in a deterioration of the image reproduction especially when the processing liquid becomes exhausted.

Finally the amount of silver halide in the photographic material could also be reduced so that less processing liquid would be necessary for development per square meter of imaging elements. Attempts of the inventors in this direction showed that especially at high temperature the image quality becomes very poor i.e. a large drop of gradation and sharpness of the image was found. Further upon reduction of the amount of silver halide in the photographic material the speed of such photographic material decreases which would make the material unsuitable for some applications.

## 3. Summary of the invention.

According to the present invention it is an object to provide an imaging element that can yield images of high quality in a silver salt diffusion transfer process even when the processing liquid used for development becomes exhausted.

According to the present invention it is an object to provide a method for obtaining images of high quality i.e. high density, contrast, sharpness and resolution etc. according to the silver salt diffusion transfer process using an imaging element that consumes less processing liquid and that can yield images of a desired quality even when the processing liquid becomes exhausted.

According to the present invention there is provided an imaging element comprising on a support (i) a photosensitive layer containing an amount of silver halide expressed as AgNO<sub>3</sub> between 0.6g/m<sup>2</sup> and 2g/m<sup>2</sup>

and hydrophilic colloid in a total amount between  $0.5\text{g/m}^2$  and  $2\text{g/m}^2$ , (ii) an anti-halation substance and (iii)  $\text{TiO}_2$  provided under the photosensitive layer of the imaging element when viewed from its photosensitive side.

According to the present invention there is provided a method for obtaining images with the above  
5 defined imaging element.

#### 4. Detailed description of the invention.

It has been found that with the above described imaging element images of high density, sharpness  
10 and resolving power can be obtained when said imaging element is developed according to the silver salt diffusion transfer process whilst in contact with an image receiving layer despite the thin silver halide emulsion layer used. Especially under conditions where the processing liquid used for development is in use for some time, the image quality remains good.

According to the present invention an antihalation substance and  $\text{TiO}_2$  pigment, preferably rutile  $\text{TiO}_2$   
15 pigment, are provided under the photosensitive layer of the imaging element when it is viewed from the photosensitive side. Preferably the antihalation substance and  $\text{TiO}_2$  are arranged in separate hydrophilic layers containing hydrophilic colloid such that the layer containing  $\text{TiO}_2$  is located between the photosensitive layer and the layer containing an antihalation substance. When the support is transparent the antihalation substance can be provided in a backing layer contained on the side of the support opposite to  
20 the side of the support containing the photosensitive layer. Said backing layer can optionally be covered with an outermost white layer containing white pigments. According to a further alternative the antihalation substance can be provided in the support itself.

Suitable antihalation substances for use in connection with the present invention are substances that are capable of substantially absorbing the light used for exposing the imaging element. For this purpose dyes  
25 or mixtures of dyes can be used. A preferably used antihalation substance is carbon black. The antihalation substance is preferably provided in amounts sufficient to obtain an optical density of the layer containing the antihalation substance between 0.3 and 2.0 more preferably between 0.3 and 1.8 and most preferably between 0.4 and 1.6.

The  $\text{TiO}_2$  pigment used in connection with the present invention may be provided in the imaging  
30 element also called photographic material in amounts between  $0.05\text{ g/m}^2$  and  $15\text{ g/m}^2$  more preferably between  $1\text{g/m}^2$  and  $5\text{g/m}^2$ .

The photosensitive layer according to the present invention contains silver halide expressed as  $\text{AgNO}_3$   
between  $0.6\text{g/m}^2$  and  $2.0\text{g/m}^2$  and hydrophilic colloid in a total amount between  $0.5\text{g/m}^2$  and  $2\text{g/m}^2$ . More preferably the amount of silver halide is between  $0.7\text{g/m}^2$  and  $1.4\text{g/m}^2$ . The amount of hydrophilic colloid is  
35 more preferably between  $0.5\text{g/m}^2$  and  $1.5\text{g/m}^2$ .

The hydrophilic colloid binder contained in the photosensitive layer and other hydrophilic layers such as e.g. a layer containing the antihalation substance and/or  $\text{TiO}_2$  is preferably gelatin. But instead of or  
together with gelatin, use can be made of one or more other natural and/or synthetic hydrophilic colloids, e.g. albumin, casein, zein, polyvinyl alcohol, alginic acids or salts thereof, cellulose derivatives such as  
40 carboxymethyl cellulose, modified gelatin, e.g. phthaloyl gelatin etc.

The total amount of hydrophilic colloid contained on the photosensitive side of the support of the imaging element in accordance with the present invention is preferably kept at a minimum. Preferably the total amount of hydrophilic colloid on the photosensitive side will be between  $2\text{g/m}^2$  and  $9\text{g/m}^2$  and more preferably between  $4\text{g/m}^2$  and  $6\text{g/m}^2$ .

The photosensitive silver halide used in the present invention may comprise silver chloride, silver  
45 bromide, silver bromoiodide, silver chlorobromoiodide and the like, or mixtures thereof. To obtain a sufficiently high rate of solution of the silver halide and a satisfactory gradation necessary for graphic purposes a silver halide emulsion mainly comprising silver chloride is used preferably. This silver chloride emulsion may comprise silver bromide upto 40mole% preferably upto 20 mole% and/or silver iodide upto  
50 2% preferably upto 0.5%. The silver iodide is preferably contained on the surface of the silver halide grains.

The silver halide emulsions may be coarse or fine grain and can be prepared by any of the well known procedures e.g. single jet emulsions, double jet emulsions such as Lippmann 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. Surface image emulsions may be used or internal image emulsions may be used  
55 such as those described in US-A 2,592,250, 3,206,313, and 3,447,927. If desired, mixtures of surface and internal image emulsions may be used as described in US-A 2,996,382.

The silver halide particles of the photographic emulsions may have a regular crystalline form such as cubic or octahedral form or they may have a transition form. Regular-grain emulsions are described e.g. in

J. Photogr. Sci., Vol. 12, No. 5, Sept./Oct. 1964, pp. 242-251. 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 shell of different halide composition. Besides having a differently  
 5 composed core and shell the silver halide grains may comprise also different halide compositions and metal dopants inbetween.

The average size expressed as the average diameter of an equivalent sphere of the silver halide grains may range from 0.2 to 1.2  $\mu\text{m}$ , preferably between 0.2 $\mu\text{m}$  and 0.8 $\mu\text{m}$ , and most preferably between 0.3 $\mu\text{m}$  and 0.6 $\mu\text{m}$ . The size distribution can be homodisperse or heterodisperse. A homodisperse size distribution is  
 10 obtained when 95 % of the grains have a size that does not deviate more than 30 % from the average grain size.

The emulsions 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-A 493,464 and 568,687, and polyamines such as diethylene  
 15 triamine or derivatives of aminomethane-sulphonic acid can be used as chemical sensitizers. Other suitable chemical sensitizers are noble metals and noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium. This method of chemical sensitization has been described in the article of R.KOSLOWSKY, Z. Wiss. Photogr. Photophys. Photochem. 46, 65-72 (1951).

The emulsions can also be sensitized with polyalkylene oxide derivatives, e.g. with polyethylene oxide  
 20 having a molecular weight of 1000 to 20,000, or with condensation products of alkylene oxides and aliphatic alcohols, glycols, cyclic dehydration products of hexitols, alkyl-substituted phenols, aliphatic carboxylic acids, aliphatic amines, aliphatic diamines and amides. The condensation products have a molecular weight of at least 700, preferably of more than 1000. It is also possible to combine these sensitizers with each other as described in BE-A 537,278 and GB-A 727,982.

The spectral photosensitivity of the silver halide can be adjusted by proper spectral sensitization by means of the usual mono- or polymethine dyes such as acidic or basic cyanines, hemicyanines, oxonols, hemioxonols, styryl dyes or others, also tri- or polynuclear methine dyes e.g. rhodacyanines or  
 25 neocyanines. Such spectral sensitizers have been described by e.g. F.M. HAMER in "The Cyanine Dyes and Related Compounds" (1964) Interscience Publishers, John Wiley & Sons, New York.

The silver halide emulsions 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  
 30 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.

The silver halide emulsions may further contain either or not in combination with one or more developing agents pH controlling ingredients, and other ingredients such as antifogging agents, develop-  
 35 ment accelerators, wetting agents, and hardening agents for gelatin.

The silver halide emulsion coated side of the photographic material can be provided with a top layer that contains hydrophilic colloids that form a waterpermeable layer. Its nature is such that it does not inhibit or restrain the diffusion transfer of the complexed silver but acts e.g. as an anti-stress layer. Appropriate hydrophilic binding agents for such top layer are e.g. gelatin, methyl cellulose, the sodium salt of carboxymethyl cellulose, hydroxyethyl cellulose, hydroxyethyl starch, hydroxypropyl starch, sodium al-  
 40 ginate, gum tragacanth, starch, polyvinyl alcohol, polyacrylic acid, polyacrylamide, poly-N-vinyl pyrrolidinone, polyoxyethylene, and copoly (methylvinylether/maleic acid). The thickness of this layer depends on the nature of the colloid used and the required mechanical strength. Such layer if present may be transferred at least partially to the image-receiving layer without deleterious action on the image formation.

The support for the imaging element may be any opaque or transparent support. Transparent supports  
 50 are made e.g. of cellulose triacetate, polyvinyl chloride, polycarbonates, polystyrene or polyesters such as polyethylene terephthalate being provide with a suitable subbing layer(s) for adhering thereto a hydrophilic colloid layer. Opaque paper supports are usually made of paper coated with a water-impermeable layer of a polyolefine such as polyethylene.

According to the method of the present invention the above described imaging element is information-  
 55 wise or image-wise exposed to actinic radiation and is subsequently developed with an alkaline processing liquid in the presence of developing agent(s) and silver halide solvent(s) whilst in contact with an image receiving material.

The image receiving material contains on a support an image receiving layer containing physical development nuclei. Suitable physical development nuclei for use in accordance with the present invention are those commonly employed in the DTR-process e.g. noble metal nuclei e.g. silver, palladium, gold, platinum, sulphides, selenides or telurides of heavy metals e.g. PdS, Ag<sub>2</sub>S, AgNiS, CoS etc.. Preferably used are PdS, Ag<sub>2</sub>S or AgNiS nuclei. The amount of nuclei used in the image receiving layer is preferably between 0.02 mg/m<sup>2</sup> and 10 mg/m<sup>2</sup>.

The support of the image receiving material may be opaque or transparent, e.g. a paper support or resin support.

The image receiving layer comprises for best imaging results the physical development nuclei in the presence of a protective hydrophilic colloid, e.g. gelatin and/or colloidal silica, polyvinyl alcohol etc..

Most of the 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 plugging 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 a preferred embodiment the processing liquid and/or the image-receiving element 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. In practice such can be realized by using the silver image toning agents in a coverage in the range from 1 mg/m<sup>2</sup> to 20 mg/m<sup>2</sup> in a hydrophilic waterpermeable colloid layer.

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 thiohydantoin and of the class of phenyl substituted mercapto-triazoles. Still further toning agents suitable for use in accordance with the preferred embodiment of 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 the development nuclei containing layer and/or hydrophilic colloid layer in waterpermeable relationship 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 partly 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 1 mg/m<sup>2</sup> to 20 mg/m<sup>2</sup>.

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 preferably takes 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 connection with the present invention and contains a water-impermeable support coated with (1) an image-receiving layer 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<sup>2</sup>,
- (ii) in layer (1) the coverage of the nuclei is in the range of 0.1 mg/m<sup>2</sup> to 10 mg/m<sup>2</sup>, and the coverage of binder is in the range of 0.4 to 1.5 g/m<sup>2</sup>, and
- (iii) in said top layer (2) the coverage of hydrophilic colloid is in the range of 0.1 to 0.9 g/m<sup>2</sup>.

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<sup>2</sup> of hydrophilic colloid, the total solids coverage of layers (1) and (2) together with the undercoat being at most 2 g/m<sup>2</sup>.

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<sup>2</sup>.

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.

Processing of the information-wise exposed imaging element whilst in contact with the receiving material is accomplished using an alkaline processing liquid having a pH preferably between 9 and 13. The pH of the alkaline processing liquid may be established using various alkaline substances. Suitable alkaline substances are inorganic alkali e.g. sodium hydroxide, potassium carbonate or alkanolamines or mixtures thereof. Preferably used alkanolamines are tertiary alkanolamines e.g. those described in EP-A-397925, EP-A-397926, EP-A-397927, 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 applications laid open to the public numbers 73949/61, 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.

Suitable developing agents for the exposed silver halide are e.g. hydroquinone-type and 1-phenyl-3-pyrazolidone-type developing agents as well as p-monomethylaminophenol and derivatives thereof. Preferably used is a combination of a hydroquinone-type and 1-phenyl-3-pyrazolidone-type developing agent wherein 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 449340. 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 European patent application number 498968.

The developing agent or a mixture of developing agents can be present in an alkaline processing solution, in the photographic material or the image receiving material. In case the developing agent or a mixture of developing agents is contained in the photographic material and/or image receiving material, the processing solution can be merely an aqueous alkaline solution that initiates and activates the development.

According to the present invention the imaging element is developed in the presence of a silver halide solvent. 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 4,297,430 and US 4,355,090. 2-mercaptobenzoic acid derivatives are described as silver halide solvents in US 4,297,429, preferably combined with alkanolamines or with cyclic imides and alkanolamines. Dialkylmethylenedisulfones can also be used as silver halide solvent.

The silver halide solvent is preferably present in the processing solution but may also be present in one or more layers comprised on the support of the imaging element and/or receiving 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.

The processing solution may comprise other additives such as e.g. thickeners, preservatives, detergents e.g. acetylenic detergents such as surfynol 104, surfynol 465, surfynol 440 etc. all available from Air Reduction Chemical Company New York.

The development and diffusion transfer can be initiated in different ways e.g. by rubbing with a roller that has been wetted with the processing liquid, e.g. acts as meniscus coater, by wiping with an absorbent means e.g. with a plug of cotton or sponge, or by dipping the material to be treated in the liquid composition. Preferably, they proceed in an automatically operated apparatus such as the COPYPROOF (registered trade name of AGFA-GEVAERT N.V. Belgium) type CP 38, CP 380, CP 42 or CP 530 processors. The DTR-process is normally carried out at a temperature in the range of 10 °C to 35 °C.

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

## EXAMPLE 1

## Preparation of the imaging elements

## 5 Sample 1

A polyethylene terephthalate film support having a thickness of 0,1 mm being coated at both sides with a subbing layer, was coated with an antihalation layer on the basis of carbon black dispersed in gelatin wherein also hydroquinone and 1-phenyl-4-methyl-pyrazolidin-3-on were present at a coverage of 0.57 g/m<sup>2</sup> and 0.32 g/m<sup>2</sup> respectively. The gelatin coverage in this antihalation layer was 3.8 g/m<sup>2</sup>. On said antihalation layer an orthochromatically sensitized negative working gelatine silver halide emulsion layer containing an amount of silver chlorobromide (1.8 mol % bromide) equivalent to 1.95 g/m<sup>2</sup> of silver nitrate was coated. The average grain size of the silver chlorobromide was 0.3 microns. The gelatin/silver nitrate weight ratio in this emulsion layer was 1.36. The silver halide emulsion layer was overcoated with a thin protective gelatin layer having a thickness of 0.5μm.

On the rear side of the film support there was provided a gelatin layer in order to prevent curling.

## Sample 2

An imaging element was prepared as described for sample 1 with the exception that the gelatin coverage in the carbon black containing antihalation undercoat layer was reduced to 3 g/m<sup>2</sup>. On said undercoat layer was coated the silver halide emulsion layer equivalent to 1.3 g/m<sup>2</sup> of silver nitrate. The gelatin/silver weight ratio in the emulsion layer was 0.97.

## 25 Sample 3

An imaging element was prepared as described for sample 1 with the difference that on the undercoat layer containing carbon black and gelatin at a coverage of 3.8 g/m<sup>2</sup>, there was coated the silver halide emulsion layer equivalent to 1.3 g/m<sup>2</sup> silver nitrate. The gelatin/silver weight ratio was 0.76.

## 30 Sample 4

An imaging element was prepared as described for sample 1 with the difference that on the undercoat layer containing carbon black and gelatin in a coverage of 3.8 g/m<sup>2</sup> there was coated a silver halide emulsion layer equivalent to 1.3 g/m<sup>2</sup> silver nitrate. The weight ratio gelatin/silver was in this case 0.97.

## Sample 5

A polyethyleneterephthalate film support was coated on one side with an undercoat layer containing rutile TiO<sub>2</sub> pigment at a coverage of 2.5 g/m<sup>2</sup> and dispersed in gelatin.

Hydroquinone and 1-phenyl-4-methyl-pyrazolidin-3-on were present at a coverage of 0.57 and 0.32 g/m<sup>2</sup> respectively. The gelatin coverage was 3 g/m<sup>2</sup>. On said undercoat layer an orthochromatically sensitized negative working gelatin silver halide emulsion layer containing an amount of silver chlorobromide (1.8 mol % bromide) equivalent to 1.95 g/m<sup>2</sup> of silver nitrate was coated. The average grain size of the silver chlorobromide was 0.3 microns.

The gelatin/silver weight ratio in this emulsion layer was 1.36. The silver halide emulsion was overcoated with a thin protective gelatine layer.

The back side of the film support was provided with an antihalation layer on the basis of carbon black dispersed in gelatin (0.66 g/m<sup>2</sup> carbon black).

## 50 Sample 6

An imaging element was prepared as described for sample 5 however the silver halide emulsion layer was coated in an amount equivalent to 1.3g/m<sup>2</sup> of silver nitrate and the gelatin/silver ratio was 0.76.



## Sample 7

An imaging element was prepared as described for sample 5 however the silver halide emulsion layer was coated equivalent to 1.3 g/m<sup>2</sup> of silver nitrate whereas the gelatin/silver ratio was 0.97.

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Preparation of an image-receiving material.

One side of a paper support having a weight of 110 g/m<sup>2</sup> and being coated at both sides with a polyethylene layer was coated at a dry coverage of 2 g/m<sup>2</sup> 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<sup>2</sup> and a top layer was provided of 0.7 g of gelatin per m<sup>2</sup>.

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Exposure procedure

The photographic materials were exposed through a sensitometric wedge in a contact exposure apparatus operating with a light source having a colour temperature of 3.200 ° K.

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DTR-transfer procedure

The exposed photographic materials were pre-moistened with the hereinafter defined 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 30 seconds. Several transfers were carried out at different processing liquid temperatures being 14, 22 and 30 ° C respectively.

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Composition of the processing liquid

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Water	800 ml
Hydroxyethylcellulose	1 g
Ethylenediaminetetraacetic acid tetrasodium salt	2 g
Na <sub>2</sub> SO <sub>3</sub> (anhydrous)	45 g
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (anhydrous)	14 g
KBr	0.5 g
1-Phenyl-5-mercapto-tetrazole	0.1 g
1-(3,4-Dichlorophenyl)-1H-tetrazole-5-thiol	0.02 g
N-methyl-ethanolamine	45 ml
N-methyl-diethanolamine	30 ml
Water up to	1.000 ml

The obtained test wedge prints on the image-receiving material were evaluated with regard to maximum density ( $D_{\max}$ ) and gradation (gamma-value), the results of which are listed in table 1.

## 45 Evaluation

For the DTR-prints obtained on the paper base image-receiving material the maximum reflection density was measured ( $D_{\max}$ ), and the gamma value (maximum gradient of the straight line portion of the sensitometric curve). The reflection density measurement proceeded according to American National Standard for Photography (Sensitometry) ANSI PH2.17-1985.

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Table 1

no.	Undercoat layer		Emulsion layer		Tot.	D <sub>max</sub>			Gradation		
	Gel.	TiO <sub>2</sub>	AgX	Gel.	Gel.	14°C	22°C	30°C	14°C	22°C	30°C
1	3.8	–	1.95	2.67	6.97	2.11	2.04	1.82	18.3	19.9	24.7
2	3.0	–	1.30	1.27	4.77	2.01	2.05	2.11	23.5	29.0	28.8
3	3.8	–	1.30	1.00	5.30	1.95	1.92	1.86	18.2	16.4	18.7
4	3.8	–	1.30	1.27	5.57	2.05	1.98	1.84	19.2	17.0	17.8
5	3.0	+	1.95	2.67	6.17	2.03	2.00	1.87	26.0	27.9	31.3
6	3.0	+	1.30	1.00	4.50	2.03	1.98	1.85	24.9	22.6	25.6
7	3.0	+	1.30	1.27	4.77	2.01	1.98	1.90	24.1	22.7	25.9

In the above table Gel. represents the amount of gelatine (g/m<sup>2</sup>) in each of the layers, AgX represents the amount of silver halide expressed in g/m<sup>2</sup> of AgNO<sub>3</sub> and Tot. represents the total amount of gelatin on the photosensitive side of the imaging element.

## EXAMPLE 2

Each day during 8 days 20 imaging elements (A<sub>4</sub>-size) of samples 1 and 7 were processed with the image receiving material described in example 1 using the processing liquid described in example 1. For each of the samples there was started with a fresh processing liquid. It was found that the maximum density of the comparative sample 1 dropped from 2.03 initially in a fresh processing liquid to 1.73 after 8 days using said processing liquid. For sample 7, according to the invention, the drop of the maximum density was only from 2.03 initially to 1.94 after 8 days.

## Claims

1. An imaging element comprising on a support (i) a photosensitive layer containing an amount of silver halide expressed as AgNO<sub>3</sub> between 0.6g/m<sup>2</sup> and 2.0g/m<sup>2</sup> and hydrophilic colloid in a total amount between 0.5g/m<sup>2</sup> and 2.0g/m<sup>2</sup>, (ii) an anti-halation substance and (iii) TiO<sub>2</sub> provided under the photosensitive layer of the imaging element when viewed from its photosensitive side.
2. An imaging element according to claim 1 wherein said antihalation substance and TiO<sub>2</sub> pigment are arranged in two separate hydrophilic layers containing a hydrophilic colloid and wherein the layer containing the TiO<sub>2</sub> pigment is located between the layer containing said antihalation pigment and said photosensitive layer.
3. An imaging element according to claim 1 wherein said antihalation substance is incorporated in said support of said imaging element and said TiO<sub>2</sub> pigment is present in a hydrophilic layer between said support and said photosensitive layer.
4. An imaging element according to claim 2 wherein said support is a transparent support and said layer containing said antihalation pigment is provided on the side of said support opposite to the side containing said photosensitive layer.
5. An imaging element according to any of the preceding claims wherein said amount of hydrophilic colloid in said photosensitive layer is between 0.5g/m<sup>2</sup> and 1.5g/m<sup>2</sup>.
6. An imaging element according to any of the preceding claims wherein the total amount of hydrophilic colloid on the photosensitive side of said imaging element is between 4 and 6g/m<sup>2</sup>.

7. A method for obtaining an image comprising the steps of information-wise exposing an imaging element as defined in any of the preceding claims to actinic radiation and developing a thus obtained information-wise exposed imaging element in the presence of developing agent(s) and silver halide solvent(s) whilst in contact with an image receiving material containing on a support an image receiving layer containing physical development nuclei.

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## EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0410

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)
Y	US-A-4 144 064 (L.L. VERMEULEN ET AL.) * column 3, line 6 - line 17 * * column 7, line 32 - line 36; claims; example 1 * ---	1-7	G03C8/06 G03C1/95
Y	US-A-5 057 395 (Y.TSUBAI ET AL) * column 7, line 54 - line 63; example 1 * * column 9, line 56 - column 10, line 40; examples 2,3; tables 2,3 * ---	1-7	
Y	DE-A-3 435 792 (MITSUBISHI PAPER MILLS) * page 23, line 31 - page 24, line 4; example 1 * ---	1,5-7	
Y	DATABASE WPIL Section Ch, Week 8214, Derwent Publications Ltd., London, GB; Class G06, AN 8227464E & JP-A-57 035 854 (MITSUBISHI PAPER MILLS) 26 February 1982 * abstract * ---	1-7	
D,A	EP-A-0 402 523 (MITSUBISHI PAPER MILLS) -----		TECHNICAL FIELDS SEARCHED (Int. Cl.5)  G03C G03F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29 JUNE 1993	Examiner PHILOSOPH L.
<b>CATEGORY OF CITED DOCUMENTS</b>			
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	