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## (54) A silver halide imaging material and a method for obtaining an image according to the silver salt diffusion transfer process.

(57) The present invention provides a method for obtaining an image according to the silver salt diffusion transfer process comprising the steps of:

- image-wise exposing an imaging material comprising on a support a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and a waterpermeable top layer, that is essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer,
- developing said imaging material whilst in contact with an image receiving material comprising on a support an image receiving layer containing physical development nuclei using an aqueous alkaline processing solution in the presence of developing agent(s) and silver halide solvent(s) and
- separating said imaging material and image receiving material from each other,

characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 $g/m^2$ and in that the coverage of the hydrophilic colloids comprised in said photosensitive layer is not more than 2.4 $g/m^2$.

The invention also provides an imaging material comprising a silver halide emulsion layer in water permeable contact with a water permeable base layer and a water permeable top layer which comprises not more than 0.4$g/m^2$ hydrophilic colloids.

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1. Field of the invention.

The present invention relates to an imaging element having a silver halide emulsion layer and to a method for obtaining an image therewith using the silver salt diffusion transfer method.

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 US-P 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-image can be formed in the image-receiving layer of a sheet or web material which is a separate element with respect to the photographic silver halide emulsion material (a so-called two-sheet DTR element) or in the image-receiving layer of a so-called single-support-element. also called mono-sheet element, which contains at least one photographic silver halide emulsion layer integral with an image-receiving layer in water permeable relationship therewith. 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 material, hereinafter also called negative material, having a photosensitive silver halide emulsion layer is brought into close contact with an image-receiving material, hereinafter also called 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 formed with a high transfer speed.

Many attempts have been made to improve said properties of the silver image. Most of these attempts were related to the composition of the positive material. Indeed, the influence of the positive material on the afore-mentioned properties of the silver image has been recognized for years (ref. the already mentioned book of A. Rott and E. Weyde, p. 48 -54, 61). So, it is disclosed in e.g. EP-A 218,752, 546,598 and 546,599 that the density of the silver image can be improved by adding specified ingredients to the positive material. It is furthermore disclosed in EP-A 306,561 that a silver image with a higher density, a better tone and a high transfer speed is obtained with a specified composition and layer thickness of the positive material.

The influence of the negative material on the afore-mentioned properties of the silver image seems to be restricted. The important role of the silver halide content of the emulsion layer on the maximum density of the silver image has been mentioned (ref. the already mentioned book of A. Rott and E. Weyde. p. 45). In US-P 5.057.395 it has been described that the tone of the silver image and the running characteristics of a processing liquid can be improved by using an imaging element consisting of a base-layer and an emulsion layer, and an image-receiving element, each with a specified composition, in the presence of specified organic compounds. In EP-A 402.523 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 of an imaging element consisting of a base-layer and an emulsion layer between 6 and 8g/m$^2$ while keeping the swelling ratio between 3.5:1 and 5.5:1. In EP-A 93200410.4 it has been described that the running characteristics of a processing liquid can be improved by using a imaging element, conprising a base-layer and an emulsion layer with a specified composition.

The influence of the processing liquid on the afore-mentioned properties of the silver image has also been examined. Most of the DTR-processing solutions now available on the market and suitable for obtaining a silver image according to the above-described method comprise alkanolamines. Such solutions,

having a favourable influence on one or more of said properties are disclosed in e.g. US-P 4,568,634, 4,632,896, EP-A 496,126 and JP Pi 61-73954, 61-73953 and 61-73949. However, alkanolamines are ecologically suspected compounds and have an unpleasant smell.

So, in spite of all these teachings, there remains a need for a silver salt diffusion transfer material improved for one or more of the above-mentioned properties.

## 3. Summary of the invention.

It is an object of the present invention to provide a method for obtaining an image of high density and high transfer speed in a wide range of processing conditions using the silver salt diffusion transfer process.

It is a further object of the present invention to provide a silver salt diffusion transfer material for making images of high density and high transfer speed in a wide range of processing conditions.

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

According to the present invention there is provided a method for obtaining an image according to the silver salt diffusion transfer process comprising the steps of:

- image-wise exposing an imaging material comprising on a support a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and a waterpermeable top layer, that is essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer,
- developing said imaging material whilst in contact with an image receiving material comprising on a support an image receiving layer containing physical development nuclei using an aqueous alkaline processing solution in the presence of developing agent(s) and silver halide solvent(s) and
- separating said imaging material and image receiving material from each other,

characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 g/m$^2$ and in that the coverage of the hydrophilic colloids comprised in said photosensitive layer is not more than 2.4 g/m$^2$.

According to the present invention there is also provided an imaging material comprising on a support a waterpermeable base layer comprising a hydrophilic colloid, a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and being in waterpermeable contact with said waterpermeable base layer and a waterpermeable top layer, that is essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 g/m$^2$.

## 4. Detailed description of the invention

It has been found that when an imaging material comprising on a support a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and a waterpermeable top layer, essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 g/m$^2$ and in that the coverage of the hydrophilic colloids comprised in said photosensitive layer is not more than 2.4 g/m$^2$, the quality of the obtained image using the DTR-process is improved. Especially the density and the speed of transfer are improved. The DTR-material according to the present invention further offers the advantage that it can be used in a wide range of processing conditions without a substantial loss of image quality.

The nature of a waterpermeable layer is such that it does not substantially inhibit or restrain the diffusion of water or of compounds contained in an aqueous solution e.g. developing agents or the complexed silver. Layers being in waterpermeable contact with each other are layers that are contiguous to each other or only separated from each other by (a) waterpermeable layer(s).

The coverage of the hydrophilic colloid(s) of the waterpermeable top layer, that is essentially free from silver halide emulsion depends on the nature of the colloid(s) used and the required mechanical strength but is in the present invention not more than 0.4 g/m$^2$. Essentially free from silver halide emulsion means that said top layer contains less than 0.1 g/m$^2$ , preferably none silver halide emulsion. Such top layer does not inhibit or restrain the diffusion transfer of the complexed silver but acts as an anti-stress layer, as a protective layer against mechanical damage of the imaging element during handling, as a layer improving the contact between the negative and the positive materials during processing, etc.. Such layer may be transferred at least partially to the image-receiving layer without deleterious action on the image formation.

In the imaging material according to the present invention, the photosensitive silver halide emulsion layer can be coated from any photosensitive silver halide emulsion comprising a hydrophilic colloid binder

provided the coverage of hydrophilic colloid contained in said layer is not more than 2.4 g/m$^2$, more preferably not more than 2.2 g/m$^2$. The weight ratio of hydrophilic colloid binder to silver halide expressed as equivalent amount of silver nitrate to binder is preferably in the range of 3:1 to 1:3 .

It is further preferred that the sum of the coverage of the hydrophilic colloids contained in said top layer, that is essentially free from silver halide emulsion and the emulsion layer is not more than 2.5 g/m$^2$, more preferred not more than 2.2 g/m$^2$.

The photosensitive silver halide used in the present invention may be any type of photographic silver halide emulsion material suited for use in diffusion transfer reversal processing, preference being given to silver halide emulsion layers the silver halide of which is mainly silver chloride because of its relatively easy complexing with thiosulphate ions. The silver halide grains can have any size or shape and may be prepared by any technique known in the art, e.g. by single-jet or double jet precipitation. Negative type or direct-positive type silver halide grains may be used. Negative and positive working type silver halide emulsions are known in the art and are described e.g. in Research Disclosure, November 1976, item 15162.

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 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 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.

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, development accelerators, wetting agents, and hardening agents for gelatin.

The silver halide emulsion layer may comprise light-screening dyes that absorb scattering light and thus promote the image sharpness and, as a consequence thereof, the sharpness of the final printed copy. Light-absorbing dyes that can be used as light-screening dyes have been described in i.a. US-P 4,092,168, 4,311,787, DE-A 2,453,217 and GB-A 1,907,440. 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 imaging element of the present embodiment may contain other additional layers comprising a hydrophilic colloid in waterpermeable relationship with the silver halide emulsion layer. Preferably, the total sum of the coverage of the hydrophilic colloids comprised in the photosensitive layer and in all other layers of the imaging material comprising a hydrophilic colloid and being in waterpermeable contact with the photosensitive layer is not more than 6.3 g/m$^2$, more preferably not more than 5.6 g/m$^2$.

It is especially advantageous to include a base-layer between the support and the photosensitive silver halide emulsion layer. Preferably, the sum of the coverage of the hydrophilic colloids contained in said base layer, the top layer, that is essentially free from silver halide emulsion and and the emulsion layer is not more than 6 g/m$^2$, more preferably not more than 5.5 g/m$^2$. In a preferred embodiment of the present invention said base-layer serves as an antihalation layer so that the reflectance of the support containing said antihalation layer is not more than 25% and preferably not more than 15%. This layer can therefore 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. Alternatively the support it self may be selected such that it can serve as antihalation means as described in e.g. US-P 4,165,237. 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. At least part of these matting agents and/or light reflection pigments may also be present in the silver halide emulsion layer the most part however preferably being present in said base-layer. As a further alternative the light reflecting pigments may be present in a separate layer provided between the antihalation layer and the photosensitive silver halide emulsion layer.

The hydrophilic colloid binder, which is comprised in the various layers of the imaging material, is usually 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 carboxymethyl cellulose, modified gelatin, e.g. phthaloyl gelatin etc.. The nature of the binder is such that the amount of liquid taken up by the imaging element when soaked for 1 min. in a 0.1 N aqueous solution of NaOH is preferably between 3.5 ml and 7 ml for 1 g binder.

The support for the imaging element may be any opaque or transparent support. Transparent supports 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.

In a preferred embodiment in connection with the present invention a backing layer is provided at the non-light sensitive side of the support. This layer which can serve as anti-curl layer can contain i.a. matting agents e.g. silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g. titanium oxide and the usual ingredients like hardeners and wetting agents. The backing layer can consist of one single layer or a double layer pack.

The imaging material can be used in conjunction with any type of image-receiving material suited for use in diffusion transfer reversal processing, said image-receiving material comprising on at least one side of the support an image receiving layer containing physical development nuclei.

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

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 of e.g. silver, palladium, gold, platinum and sulphides, selenides or tellurides of heavy metals e.g. PdS, $Ag_2S$, AgNiS, CoS etc.. Preferably used are $Ag_2S$ or AgNiS nuclei.

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.

The coverage of said nuclei is preferably in the range of 0.1 mg/m$^2$ to 10 mg/m$^2$, and the coverage of binder is preferably in the range of 0.4 to 1.5 g/m$^2$.

The image-receiving element may contain in operative contact with the development nuclei thioether compounds, e.g. those described in DE-P 1,124,354, in US-P 4,013,471 and 4,072,526, and in EP-A 026,520.

Most of the DTR-positive materials now available on the market comprises two or even three layers on the side of the support that contains an image receiving layer . Such materials normally contain on top of a nuclei containing layer a layer which itself preferably contains no nuclei and mainly serves to ensure good contact between the negative and positive material during transfer. Preferably, such top layer comprises a matting agent as is disclosed in e.g. EP-A 584407.

The transfer behaviour of the complexed silver largely depends on the thickness of the image-receiving layer and upperlying layers and on the kind of binding agent or the mixture of binding agents used in said layers. 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. For this reason the sum of the coverage of the hydrophilic colloids contained in said image receiving layer and said top layer is preferably less than 2 g/m$^2$ and most preferably not more than 1.8 g/m$^2$ and the coverage of the hydrophilic colloids contained in said top layer is preferably less than 0.45 g/m$^2$.

The sum of the coverage of the hydrophilic colloids contained in the top layers of the image-receiving element and the imaging element is preferably not more than 0.80 g/m$^2$.

According to a particular embodiment the nuclei containing layer is present on a nuclei-free waterpermeable underlying undercoat layer or undercoat layer system comprising a hydrophilic colloid and having preferably a coverage in the range of 0.05 to 1 g/m$^2$ of hydrophilic colloid

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 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 and/or in said top layer and/or in the undercoat layer gelatin is used preferably as hydrophilic colloid. In the image-receiving layer 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.

In at least one of the layers of the present image-receiving material substances can be contained, which play a role in the determination of the colour tone of the diffusion transfer silver image. Substances providing a neutral colour tone are called black-toning agents, e.g. as described in GB A 561,875 and BE A 502,525.

According to a preferred embodiment the processing liquid that will be described in detail below and/or the image-receiving material 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 $mg/m^2$ to 20 $mg/m^2$ 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.

Still further toning agents suitable for use in accordance with the preferred embodiment of the present invention are the toning agents described in EP-A 218752, 208346, 218753, 546599 and US-P 4.683189.

According to a practical embodiment in the image-receiving element the development nuclei containing layer and/or hydrophilic colloid layer in waterpermeable relationship therewith 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).

When applying an optical brightening agent in the present 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.

The hydrophilic colloid comprising layers of the present image-receiving material and imaging material may have been hardened 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. Hardening can also be effected by incorporating a hardener precursor in said layers, the hardening of the hydrophilic colloid therein being triggered by the treatment with the alkaline processing liquid. 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.

The silver complex diffusion transfer reversal processing is by nature a wet processing including development of the exposed silver halide in the emulsion layer of the photosensitive element, the complexing of residual undeveloped silver halide and the diffusion transfer of the silver complexes into the image-receiving material wherein physical development takes place.

The processing proceeds in alkaline aqueous medium.

The developing agent or a mixture of developing agents can be incorporated into the alkaline processing solution and/or into the imaging material. When incorporated into the photosensitive element, the developing agent(s) can be present in the silver halide emulsion layer or is (are) preferably present in a hydrophilic colloid layer in water-permeable relationship therewith, e.g. in the anti-halation layer adjacent to the silver halide emulsion layer of the photosensitive element. In case the developing agent or a mixture of developing agents is in its total contained in the photosensitive element, the processing solution is merely an aqueous alkaline solution that initiates and activates the development.

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. 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 imaging material. A preferred class of 1-phenyl-3-pyrazolidone-type developing agents is disclosed in EP-A 498968.

The silver halide solvent, preferably sodium or ammonium thiosulphate, may be supplied from the non-light-sensitive image-receiving element as mentioned above, but it is normally at least partly already

present in the alkaline processing solution. When present in the alkaline processing solution, the amount of silver halide solvent is in the range of e.g. 10 g/l to 50 g/l.

Preferred alkaline substances are inorganic alkali e.g. sodium hydroxide, sodium or potassium carbonate, sodium phosphate, sodium borate or alkanolamines or mixtures thereof. Preferably used alkanolamines are tertiary alkanolamines e.g. those described in EP-A 397925, 397926, 397927, 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, 4,568,634 etc.. The concentration of these alkanolamines is preferably from 0.1 mol/l to 0.9 mol/l.

The alkaline processing solution usually contains preserving agents e.g. sodium sulphite, thickening agents e.g. hydroxyethylcellulose and carboxymethylcellulose, fog-inhibiting agents such as potassium bromide, black-toning agents especially heterocyclic mercapto compounds, detergents e.g. acetylenic detergents such as SURFYNOL 104, SURFYNOL 465, SURFYNOL 440 etc. all available from Air Reduction Chemical Company, New York, USA.

The DTR-process is normally carried out at a temperature in the range of 10 °C to 35 °C.

The pH of the processing solution is preferably in the range of 9 to 14, more preferably in the range of 10 to 13.

For particulars about exposure and developing apparatus, which may be applied in the DTR-process according to the present invention reference is made e.g. to the above-mentioned book by A. Rott and E. Weyde and to patent literature cited therein.

The image receiving elements according to the present invention are particularly suited for the reproduction of documents or the preparation of black copies. They can be used likewise for the reproduction of line and screen images and for the production of identification documents according to the DTR-process as described in EP-A 584407.

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

EXAMPLE 1 (Comparative example)

Preparation of imaging material N1

A paper support having a weigth of 110 g/m$^2$ being coated at both sides with a polyethylene layer and provided at one side with a pack of two backing layers was coated at the other side with an antihalation layer containing carbon black in such an amount that the optical density for visual light corresponded to 0.6 and gelatin in an amount of 3.9 g/m$^2$ and wherein also hydroquinone and 1-phenyl-4-methyl-pyrazolidin-3-one were present in a coverage of 0.57 g/m$^2$ and 0.32 g/m$^2$. On said antihalation layer an orthochromatically sensitized negative working gelatino silver halide emulsion layer was coated containing an amount of silver chlorobromide (1.8 mol % bromide) equivalent to 2.0 g/m$^2$ of silver nitrate and an amount of gelatin of 2.66 g/m2. The average grain size of the silver chlorobromide was 0.3 μm. The silver halide emulsion layer was overcoated with a thin protective gelatin layer at a coverage of 0.5 g/m$^2$.

The layer nearest to the support of the backing layer pack contained 4 g/m$^2$ of gelatin, 1.5 g/m$^2$ of a colloidal silica and 0.021 g/m$^2$ of wetting agent $F_{15}C_7$-$COONH_4$. The second backing layer contained 0.3 g/m$^2$ of gelatin, 0.5 g/m$^2$ of the antistatic agent co(tetraallyloxyethane / methacrylate / acrylic acid-K-salt) polymer and 0.05 g/m$^2$ of hardening agent triacrylformal.

Preparation of imaging material N2

Imaging material N2 was prepared similar to imaging material N1 with the exception that the gelatine coverage in the top layer was 0.4 g/m$^2$.

Preparation of imaging material N3

Imaging material N3 was prepared similar to imaging material N1 with the exception that the gelatine coverage in the antihalation layer, the silver halide emulsion layer and the top layer were respectively 2.5 g/m$^2$, 1.0 g/m$^2$ and 0.4 g/m$^2$.

Preparation of image-receiving material P1

A subbed polyethylene terephthalate film support was coated at both sides at a dry coverage of 1.77 g/m$^2$ with an image-receiving layer containing silver-nickel sulphide nuclei dispersed in gelatin. This layer was applied by slide hopper coating so that the nuclei were in an undermost coating of 1.22 g gelatin/m$^2$ and a top layer was provided of 0.55 g gelatin/m$^2$.

Preparation of image-receiving material P2

The image-receiving material P2 was prepared similar to the image-receiving material P1 with the exception that the gelatine coverage in the image-receiving layer and the top layer were respectively 0.5 g/m$^2$ and 0.4 g/m$^2$.

| Composition of the processing liquid: | A1 | A2 |
|---|---|---|
| Hydroxyethylcellulose (g) | 1 | 1 |
| EDTA (g) | 2 | 2 |
| $Na_2SO_3$ (anhydrous) (g) | 45 | 60 |
| $Na_2S_20_3$ (anhydrous) (g) | 14 | 21 |
| KBr (g) | 0.5 | 0.5 |
| 1-Phenyl-5-mercapto-tetrazole (g) | 0.08 | 0.1 |
| 1-(3,4 dichlorophenyl)-1-H-tetrazole-5-thiol (g) | 0.04 | 0.02 |
| DMEA (ml) | 30 | 0 |
| MDEA (ml) | 35 | 0 |
| Boric acid | 0 | 31 |
| Sodium hydroxide | 0 | 33.5 |
| Water up to | 1 litre | 1 litre |
| pH | 11.4 | 11.9 |
| EDTA = ethylenediaminetetraacetic acid tetrasodium salt<br>DMEA = dimethylethanolamine<br>MDEA = methyldiethanolamine | | |

The photographic materials were exposed through a sensitometric wedge in a contact exposure apparatus operating with a light source having a colour temperature of 3200 °K. The exposed photographic materials were pre-moistened with a 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. Several transfers were carried out at a processing temperature of 22 °C at different transfer contact times being 15, 30, 60 and 120 seconds respectively.

The obtained test wedge prints in the image-receiving materials were evaluated with regard to maximum density. All wedge prints were measured on a densitometer MACBETH (registered trade name) type IR 924 behind visual filter, having following wavelength (nm)/optical density (D) characteristics : 700 nm / D = 0; 600 nm / D = 0.2; 500 nm / D = 1.25; 420 nm / D = 3.0.

For the DTR-prints obtained on paper base image-receiving materials maximum reflection density was measured ($D_{max}$ R). The reflection density measurement proceeded according to American National Standard for Photography (Sensitometry) ANSI PH2.17-1985.

For the DTR-prints obtained on transparent resin film base image-receiving materials maximum transmission density was measured ($D_{max}$ T). The transmission density measurement proceeded according to American National Standard for Photography (Sensitometry) ANSI PH2.19-1986.

Evaluation:

The results listed in table 1 give the $D_{max}$ T as a function of the contacting time for the combinations of the different negative materials, positive materials and processing liquids.

Table 1

| Proc. | Neg. | Pos | Contacting time | | | |
|---|---|---|---|---|---|---|
| | | | 15 s | 30 s | 60 s | 120 s |
| A1 | N1 | P1 | 1.44 | 2.62 | 3.49 | 3.88 |
| A1 | N1 | P2 | 1.74 | 2.85 | 3.63 | 4.08 |
| A1 | N2 | P1 | 1.87 | 2.93 | 3.66 | 4.06 |
| A1 | N2 | P2 | 2.11 | 3.17 | 3.83 | 4.35 |
| A1 | N3 | P1 | 2.26 | 3.38 | 3.86 | 4.28 |
| A1 | N3 | P2 | 2.57 | 3.55 | 4.12 | 4.61 |
| A2 | N1 | P1 | 1.45 | 2.28 | 2.82 | 3.02 |
| A2 | N1 | P2 | 1.51 | 2.38 | 2.95 | 3.13 |
| A2 | N2 | P1 | 1.75 | 2.68 | 2.94 | 3.20 |
| A2 | N2 | P2 | 1.86 | 2.70 | 3.04 | 3.24 |
| A2 | N3 | P1 | 2.04 | 2.97 | 3.04 | 3.40 |
| A2 | N3 | P2 | 2.23 | 3.09 | 3.29 | 3.55 |

The imaging elements N1 and N2 (comparative imaging materials) having a gelatine coverage in the top layer of 0.5 g/m$^2$ respectively 0.4 g/m$^2$ and a gelatine coverage in the emulsion layer of 2.66 g/m$^2$ show at different contact times a lower transfer speed and give images with a lower $D_{max}$ than the imaging element N3 (imaging material according to the invention) having a gelatine coverage in the top layer of 0.4 g/m$^2$ and in the emulsion layer of 1.0 g/m$^2$ . Using a positive material with a thinner top layer also helps in obtaining these properties, but not to the same extent. Indeed, particularly good results are obtained with the combination of the imaging element N3 (imaging material according to the invention) with the thin-top layer positive material P2. These results are obtained not only by using the processing liquid A1, containing alkanolamines, but also by using the processing liquid A2, which is free of alkanolamines and comprises as alkaline substance sodium borate.

EXAMPLE 2

Preparation of imaging material N4

A polyethyleneterephthalate film support (with a hydrophilic adhesion layer) of 0.1mm thickness and provided at one side with a pack of two backing layers was coated at the other side with an antihalation layer containing carbon black in such an amount that the optical density for visual light corresponded to 0.8 and gelatin in an amount of 4.7 g/m$^2$. On said antihalation layer an orthochromatically sensitized direct-positive working gelatino silver halide emulsion layer was coated containing an amount of silver chlorobromide (1.8 mol % bromide) equivalent to 2.75 g/m$^2$ of silver nitrate and an amount of gelatin of 3.26 g/m$^2$. The average grain size of the silver chlorobromide was 0.25 $\mu$m. The silver halide emulsion layer was overcoated with a thin protective gelatin layer at a coverage of 0.5 g/m$^2$.

The backing layer nearest to the support contained 4.5 g/m$^2$ of gelatin and 1.5 g/m$^2$ of carbon black. The second backing layer contained 0.6 g/m$^2$ of gelatin, 1 g/m$^2$ of the antistatic agent co(tetraallyloxyethane / methacrylate / acrylic acid-K-salt) polymer and 0.1 g/m$^2$ of hardening agent triacrylformal

Preparation of imaging material N5

Imaging material N5 was prepared similar to imaging material N4 with the exception that the gelatine coverage in the antihalation layer, the silver halide emulsion layer and the top layer were respectively 3.0 g/m$^2$, 2.0 g/m$^2$ and 0.4 g/m$^2$,

| Composition of the processing liquid: | A3 | A4 |
|---|---|---|
| Hydroxyethylcellulose (g) | 1 | 1 |
| EDTA (g) | 2 | 2 |
| $Na_2SO_3$ (anhydrous) (g) | 45 | 45 |
| $Na_2S_20_3$ (anhydrous) (g) | 14 | 21 |
| Hydroquinone | 13 | 13 |
| 1-Phenyl-4-methyl-pyrazolidin-3-one | 4.7 | 4.7 |
| KBr (g) | 0.5 | 0.5 |
| 1-Phenyl-5-mercapto-tetrazole (g) | 0.08 | 0.1 |
| 1-(3,4 dichlorophenyl)-1-H-tetrazole-5-thiol (g) | 0.04 | 0.02 |
| MMEA (ml) | 30 | 0 |
| Boric acid | 0 | 31 |
| Sodium hydroxide | 1.9 | 66 |
| Water up to | 1 litre | 1 litre |
| pH | 10.9 | 11.9 |
| EDTA = ethylenediaminetetraacetic acid tetrasodium salt<br>MMEA = monomethylethanolamine | | |

The photographic materials were exposed, processed and the obtained test wedge prints in the image-receiving materials evaluated as described in example 1 with the exception that the transfers were carried out at a processing temperature of 32 °C at contact times of 15 and 30 seconds.

Evaluation:

The results listed in table 2 give the $D_{max}$ T as a function of the contacting time for the combinations of the different negative materials, positive materials and processing liquids.

Table 2

| Proc. | Neg. | Pos | Contacting time | |
|---|---|---|---|---|
| | | | 15 s | 30 s |
| A3 | N4 | P1 | 1.44 | 2.58 |
| A3 | N4 | P2 | 1.84 | 2.98 |
| A3 | N5 | P1 | 1.94 | 3.28 |
| A3 | N5 | P2 | 2.43 | 3.63 |
| A4 | N4 | P1 | 1.45 | 2.36 |
| A4 | N4 | P2 | 1.85 | 2.74 |
| A4 | N5 | P1 | 2.10 | 2.95 |
| A4 | N5 | P2 | 2.42 | 3.17 |

The imaging element N4 (comparative imaging material) having a gelatine coverage in the top layer of 0.5 g/m$^2$ and in the emulsion layer of 3.26 g/m$^2$ shows at different contact times a lower transfer speed and gives images with a lower $D_{max}$ than the imaging element N5 (imaging material according to the invention) having a gelatine coverage in the top layer of 0.4 g/m$^2$ and in the emulsion layer of 2.0 g/m$^2$ . A positive material with a thinner top layer also helps in obtaining these properties, but not to the same extent. The best results are obtained with the combination of the imaging element N5 (imaging material according to the invention) with the thin-layer positive material P2. These results are obtained not only by using the processing liquid A3, containing an alkanolamine, but also by using the processing liquid A4, which is free of alkanolamines and comprises as alkaline substance sodium borate.

EXAMPLE 3

Preparation of imaging material N6

A polyethyleneterephthalate film support (with a hydrophilic adhesion layer) of 0.1mm thickness and provided at one side with a pack of two backing layers was coated at the other side with an antihalation layer containing carbon black in such an amount that the optical density for visual light corresponded to 0.6 and gelatin in an amount of 3.9 g/m$^2$. On said antihalation layer an orthochromatically sensitized negative working gelatino silver halide emulsion layer was coated containing an amount of silver chlorobromide (1.8 mol % bromide) equivalent to 2.5 g/m$^2$ of silver nitrate and an amount of gelatin of 3.0 g/m$^2$. The average grain size of the silver chlorobromide was 0.3 μm. The silver halide emulsion layer further contained hydroquinone and 1-phenyl-4-methyl-pyrazolidone at a coverage of 0.9 g and 0.25 g/m$^2$ respectively. The silver halide layer was then covered with a gelatin layer containing 0.5 g/m$^2$ of gelatin.

The backing layer packet was identical to the backing layer packet of imaging material N1

Preparation of imaging material N7

Imaging material N7 was prepared similar to imaging material N6 with the exception that the gelatine coverage in the antihalation layer, the silver halide emulsion layer and the top layer were respectively 3.06 g/m$^2$, 2.14 g/m$^2$ and 0.33 g/m$^2$,

Preparation of imaging material N8

Imaging material N8 was prepared similar to imaging material N1 with the exception that the gelatine coverage in the antihalation layer, the silver halide emulsion layer and the top layer were respectively 2.6 g/m$^2$, 1.86 g/m$^2$ and 0.35 g/m$^2$,

Preparation of image-receiving material P3

The image-receiving material P3 was prepared similar to the image-receiving material P1 with the exception that the gelatine coverage in the image-receiving layer and the top layer were respectively 1.4 g/m$^2$ and 0.4 g/m$^2$,

Preparation of image-receiving material P4

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 1.7 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/m$^2$ and a top layer was provided of 0.4 g of gelatin/m$^2$.

| Composition of the processing liquid: | A5 | A6 |
|---|---|---|
| Hydroxyethylcellulose (g) | 1 | 1 |
| EDTA (g) | 2 | 2 |
| $Na_2SO_3$ (anhydrous) (g) | 45 | 45 |
| $Na_2S_20_3$ (anhydrous) (g) | 14 | 21 |
| KBr (g) | 0.5 | 0.5 |
| Hydroquinone | 13 | 0 |
| 1-Phenyl-4-methyl-pyrazolidin-3-one | 4.7 | 0 |
| 1-Phenyl-5-mercapto-tetrazole (g) | 0.08 | 0.1 |
| 1-(3,4 dichlorophenyl)-1-H-tetrazole-5-thiol (g) | 0.04 | 0.02 |
| $Na_3PO_4.12H_2O$ | 20 | 0 |
| $Na_2CO_3$ | 20 | 30 |
| Water up to | 1 litre | 1 litre |
| pH | 11.3 | 10.9 |
| EDTA = ethylenediaminetetraacetic acid tetrasodium salt | | |

The photographic materials were exposed, processed and the obtained test wedge prints in the image-receiving materials evaluated as described in example 1 with the exception that the transfer contact time was 20 seconds for the paper type image receiving material P4 and 60 seconds for the resin film type image receiving materials P1 and P3 and that transfers were carried out at different processing liquid temperatures being 16, 22 and 32 °C respectively.

For the evaluation of the exhaustion of the processing liquid the following procedure was used. During 5 days each day 20 $m^2$ of a combination of an imaging material with an image-receiving material were processed at 22 °C and with contact times as above mentioned in an unrefreshed processing liquid and the obtained test wedge prints in the image-receiving materials evaluated.

Evaluation:

The results listed in table 3 give the $D_{max}$ T as a function of the processing temperature for the combinations of the different negative materials, positive materials and fresh processing liquids.

Table 3

| Proc. | Neg. | Pos | Processing temperature | | |
|---|---|---|---|---|---|
| | | | 16 °C | 22 °C | 32 °C |
| A5 | N6 | P1 | 3.02 | 3.58 | 3.74 |
| A5 | N7 | P1 | 3.34 | 3.79 | 3.85 |
| A5 | N7 | P3 | 3.70 | 4.05 | 4.12 |
| A6 | N6 | P1 | 2.73 | 3.41 | 3.78 |
| A6 | N7 | P1 | 3.48 | 3.97 | 4.31 |
| A6 | N7 | P3 | 3.85 | 4.30 | 4.41 |

The results listed in table 4 give the $D_{max}$ T as a function of the exhaustion of the processing liquid for the combinations of the different negative materials, positive materials and processing liquids.

Table 4

| Proc. | Neg. | Pos | Amount processed material | | |
|---|---|---|---|---|---|
| | | | 0 $m^2$ | 80 $m^2$ | 100 $m^2$ |
| A5 | N1 | P4 | 2.07 | 1.69 | - |
| A5 | N8 | P4 | 2.12 | 1.89 | 1.85 |
| A6 | N6 | P1 | 3.44 | 2.51 | 2.36 |
| A6 | N7 | P1 | 4.01 | 3.36 | 2.99 |
| A6 | N7 | P3 | 4.09 | 3.35 | 3.16 |
| A6 | N1 | P4 | 2.13 | 1.75 | 1.65 |
| A6 | N8 | P4 | 2.19 | 2.01 | 1.95 |

Evaluation

The imaging element N6 (comparative imaging material) having a gelatine coverage in the top layer of 0.5 g/$m^2$ and in the emulsion layer of 3.0 g/$m^2$ shows at different contact times a lower transfer speed and gives images with a lower $D_{max}$ than the imaging element N7 (imaging material according to the invention) having a gelatine coverage in the top layer of 0.33 g/$m^2$ and in the emulsion layer of 2.14 g/$m^2$ . Using a positive material with a thinner top layer increases these effects. Particularly good results are obtained with the combination of the imaging element N7 (imaging material according to the invention) with the thin-top layer positive material P3.

Furthermore, exhaustion of the processing liquid has a less detrimental effect on $D_{max}$of the images, obtained from the imaging element N7 (imaging material according to the invention) than on $D_{max}$ of the images, obtained from the imaging element N6 (comparative imaging material) which allows a longer use of the processing liquid while still obtaining images of acceptable quality.

The same conclusion is to be drawn by comparing the imaging element N1 (comparative imaging material) having a gelatine coverage in the the top layer of 0.5 g/m$^2$ and in the emulsion layer of 2.66 g/m$^2$ with the imaging element N8 (imaging material according to the invention) having a gelatine coverage in the top layer of 0.35 g/m$^2$ and in the emulsion layer of 1.86 g/m$^2$.

As shown in this example, these beneficial results with imaging materials N7 and N8 (imaging material according to the invention) are obtained by using the processing liquids A5 (a developing solution) or A6 (an activating solution) , which are free of alkanolamines and comprises as alkaline substance sodium phosphate and/or sodium carbonate.

## Claims

1. A method for obtaining an image according to the silver salt diffusion transfer process comprising the steps of:
   - image-wise exposing an imaging material comprising on a support a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and a waterpermeable top layer, that is essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer,
   - developing said imaging material whilst in contact with an image receiving material comprising on a support an image receiving layer containing physical development nuclei using an aqueous alkaline processing solution in the presence of developing agent(s) and silver halide solvent(s) and
   - separating said imaging material and image receiving material from each other,

   characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 g/m$^2$ and in that the coverage of the hydrophilic colloids comprised in said photosensitive layer is not more than 2.4 g/m$^2$.

2. A method for obtaining an image according to claim 1 wherein the sum of the coverage of the hydrophilic colloids comprised in the photosensitive layer and in the top layer of said imaging material is not more than 2.5 g/m$^2$.

3. A method for obtaining an image according to claim 1 or 2 wherein the total sum of the coverage of the hydrophilic colloids comprised in said photosensitive layer and in all other layers of said imaging material comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer is not more than 6.3 g/m$^2$.

4. A method for obtaining an image according to claim 3 wherein said total sum is not more than 5.6 g/m$^2$.

5. A method for obtaining an image according to any of claims 1 to 4 wherein said imaging material further comprises a waterpermeable base layer comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer and wherein the sum of the coverage of the hydrophilic colloids comprised in said top layer, said photosensitive layer and said base layer is not more than 6 g/m$^2$.

6. A method for obtaining an image according to any of claims 1 to 5 wherein said image receiving material further comprises a waterpermeable top layer comprising a hydrophilic colloid and being in waterpermeable contact with said image receiving layer and wherein the sum of the coverage of the hydrophilic colloids comprised in said two layers is less than 2 g/m$^2$ and the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.45 g/m$^2$.

7. A method for obtaining an image according to any of claims 1 to 6 wherein the sum of the coverage of the hydrophilic colloids comprised in the top layer of the imaging material and of the image receiving material is not more than 0.80 g/m$^2$.

**8.** A method for obtaining an image according to any of claims 1 to 7 wherein said silver salt diffusion transfer process is carried out using an alkaline processing liquid which is free of alkanolamines and comprises as alkaline substance(s) a sodium or potassium carbonate and/or a sodium or potassium phosphate and/or a sodium or potassium borate.

**9.** An imaging material comprising on a support a waterpermeable base layer comprising a hydrophilic colloid, a photosensitive silver halide emulsion layer comprising a hydrophilic colloid and being in waterpermeable contact with said waterpermeable base layer and a waterpermeable top layer, that is essentially free from silver halide emulsion, comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer characterized in that the coverage of the hydrophilic colloids comprised in said top layer is not more than 0.4 $g/m^2$.

**10.** An imaging material according to claim 9 wherein the total sum of the coverage of the hydrophilic colloids comprised in said photosensitive layer and in all other layers of said imaging material comprising a hydrophilic colloid and being in waterpermeable contact with said photosensitive layer is not more than 6.3 $g/m^2$.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0289

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| X | GB-A-2 110 400 (FUJI PHOTO FILM CO. LTD.)<br>*table 1,sample 5*<br>* page 11, line 56; claims 1,17,18 *<br>--- | 9 | G03C1/76<br>G03C8/52 |
| X | US-A-4 530 898 (A SPIEGAL)<br>* column 4, line 55 - column 5, line 5; figure 1 *<br>--- | 9,10 | |
| A | EP-A-0 383 283 (KONICA CORPORATION)<br>* page 10, line 8 - line 14; claims 1,9,10 *<br>--- | 9,10 | |
| A | US-A-5 272 046 (S SASAOKA)<br>*table 3,sample nos. 73,76,79,82*<br>* claims 1,3,4 *<br>--- | 9,10 | |
| A | US-A-3 893 855 (J C CHARKOUDIAN)<br>* column 4, line 59 - line 62; example 4 *<br>* column 5, line 34 - line 35 *<br>--- | 1,9 | |
| A | US-A-3 383 211 (J P POELS ET AL)<br>* column 2, line 19; claims 1,4 *<br>--- | 1 | TECHNICAL FIELDS SEARCHED (Int.Cl.6)<br>G03C |
| A | GB-A-869 190 (AGFA-GEVAERT AKTIENGESELLSCHAFT)<br>* page 2, left column, line 23 - line 25; claim 1; example 2 *<br>--- | 1 | |
| A | EP-A-0 208 346 (AGFA-GEVAERT NV)<br>* example 1 *<br>--- | 1 | |
| D,A | EP-A-0 306 561 (AGFA-GEVAERT NV)<br>* page 8, line 2 *<br>--- | 1 | |
| A | US-A-3 396 018 (D J BEAVERS ET AL)<br>*example XIII,table II,13th experiment*<br>* column 1, line 51 - line 61 *<br>---<br>-/-- | 1 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 20 June 1995 | Bolger, W |

CATEGORY OF CITED DOCUMENTS

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# EUROPEAN SEARCH REPORT

Application Number
EP 95 20 0289

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
|---|---|---|---|
| A | PATENT ABSTRACTS OF JAPAN vol. 12, no. 88 (P-678) (2935) 23 March 1988 & JP-A-62 222 250 (MITSUBISHI PAPER MILLS LTD) 30 September 1987 * abstract * | 5 | |
| D,A | EP-A-0 402 523 (MITSUBISHI PAPER MILLS LTD) * claim 1 * | 5 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 20 June 1995 | Bolger, W |

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