

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 610 608 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
11.09.1996 Bulletin 1996/37

(51) Int Cl.⁶: **G03C 1/30**

(21) Application number: **93200382.5**

(22) Date of filing: **12.02.1993**

(54) **Silver halide light-sensitive photographic material for use as a laser recorded medical hardcopy material and method of processing**

Photographisches, lichtempfindliches Silberhalogenidmaterial zur Wiedergabe von medizinischen laseraufgezeichneten Bildern und Verfahren zur Verarbeitung

Matériau photographique sensible à la lumière, à base d'halogénure d'argent, pour la restitution d'images médicales enregistrées par laser et méthode de traitement

(84) Designated Contracting States:
BE DE FR GB NL

(43) Date of publication of application:
17.08.1994 Bulletin 1994/33

(73) Proprietor: **AGFA-GEVAERT
naamloze vennootschap
B-2640 Mortsel (BE)**

(72) Inventor: **Goedeweck, Rudi August,
B-2640 Mortsel (BE)**

(56) References cited:
**EP-A- 0 359 483 EP-A- 0 360 616
EP-A- 0 457 153 US-A- 5 112 731**

- **RESEARCH DISCLOSURE no. 308, December 1989, HAVANT GB , XP96175 'Photographic silver halide emulsions preparations, addenda, processing and systems' chapter: XXI Development modifiers**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

EP 0 610 608 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

1. Field of the invention.

5 This invention relates to a method for reproducing images on a silver halide light-sensitive material for medical X-ray diagnosis for use as a hardcopy of electronically stored images.

2. Background of the invention.

10 There is a trend in medical diagnosis to provide hardcopies of images, produced by electronic diagnostic techniques such as computer tomography, magnetic resonance imaging, ultrasound etc., by means of a digital laser imager, replacing rapidly the older technology of CRT printers due to several advantages. As opposed to the said analog CRT camera's, a laser imager is a digital system containing a high performance digital computer. Instead of just printing the images, the incoming images can be stored temporarily in an electronic memory and the data as well as the lay-
 15 out of the images can be manipulated before actually being printed on a film. This electronic memory offers the possibility to buffer the incoming data from several diagnostic modalities by means of an image network, which is a real advantage in comparison with e.g. CRT imaging wherein the hard copy is exposed image by image. In that case, while one examination is taking place, the imager is unavailable for others and as a result, each diagnostic unit requires a separate CRT imager.

20 The photographic hardcopy material, used in the laser imagers, combines an excellent image quality with the appropriate physical properties, necessary for an error free filmhandling by the imager. With regard to image quality, the photographic material preferably has high sharpness, a good image tone of the developed silver, and the appropriate contrast values to allow a high maximum density and crisp alphanumeric.

25 Another trend in medical imaging is the demand for rapid access of the photographic images. Especially when implemented in an image network, the access time of the laser hardcopy material should be as short as possible. Factors responsible for delayed rates at which the process proceeds may be the exposure time of the film by the laser, the transport time before exposure to the system and after exposure to an automatic processor, and the processing time, dry-to-dry, of the hardcopy material. Whereas the exposure time and transport time are dependant on specific features of the laser source, the mechanical construction of the system and the dimensions of the hardcopy material,
 30 the processing time is especially determined by the film characteristics and the chemicals used in the processing cycle. Typical modern processors have dry-to-dry cycles of less than 60 s, more preferable less than or equal to 50 seconds.

35 Last, there is a stringent demand for processing medical images in hardener free developing and fixing baths. Hardener free chemistry offers higher convenience with regard to ecology, manipulation and regeneration of chemicals in the automatic processor provided that the hardcopy material has the expected sensitometric results as e.g. sensitivity, gradation and maximum density within restricted processing time limits. The hardening agent reduces the drying time in the automatic processor by crosslinking the gelatin chains of the photographic material, thereby reducing the water adsorption of said material. Therefore, a photographic material suited for hardener free processing should be forehardened during emulsion coating in order to allow a short dry-to-dry processing cycle.

40 EP-A-0 360 616 claims a material designed for rapid processing after exposure with a laser printer. In order to reduced drying times water absorption on the emulsion side is less than 8.5 g/m². As light-sensitive silver halide emulsion crystals, use is made, e.g., of monodisperse octahedric silverbromiodide with a silver iodide content of 2 %. In EP-A-0 359 483 combinations of particular grain sizes, ratios of gelatin to silver halide and coating weights are disclosed in order to reduce the drying time without adversely affecting sensitometry. Various types of silver halide emulsions may be used therein as well as any configuration of grains in the practice of rapid processing of materials exposed by
 45 CRT or laser imaging. More specific low coating amounts of hydrophilic colloid of less than 2.5 g/m² and hardening the corresponding hydrophilic colloid layers to a degree to attain a swelling rate of less than 200 % are described in EP 0 457 153.

50 From e.g. US-Patents 3,241,640 and 5,112,731 it can be learned that flat tabular grains are preferred for a photographic material intended for hardener free processing of direct exposure X-ray images and for hardcopy images, generated by means of CRT printers. Indeed, it is well known that flat tabular grains combine a high speed with a large covering power (density vs. developed silver), even at high hardening degrees. For laser imaging however, lower speeds are required and flat tabular grains are not preferred due to the low contrast values and the brownish image tone of tabular grain emulsions.

55 3. Objects of the invention.

Therefore it is an object of this invention to provide a method for reproducing an electronically stored medical image on a photographic material for medical hardcopy by means of a laser recorder, intended for hardener free

processing within a dry-to-dry cycle time of less than 50 seconds.

4. Summary of the invention.

5 In accordance with the present invention, a medical laser hardcopy material is used, comprising a support and on only one side thereof at least one silver halide emulsion layer and at least one hydrophilic colloid layer, wherein said material has a hardening degree corresponding with a water absorption of less than or equal to 8 g/m² at the emulsion side, the said water absorption being measured as follows:

- 10
- preserving the dry film for 15 minutes in a conditioning room at 20°C and 30 % RH,
 - covering the backing topcoat layer of the dry film with a water impermeable tape,
 - weighing the dry film,
 - immersing the unexposed material in demineralized water of 24°C for 10 minutes,
 - sucking up the excessive amount of water present on top of the outermost layers and

15

 - immediately determining the weight of the wet film and
 - calculating the measured weight differences between the wet and the dry film per square meter,

and wherein said silver halide emulsion essentially consists of homogeneous cubic silver bromide or silverbromiodide crystals with at most 3 mole% of iodide ions.

20 In accordance with the present invention the method for the reproduction of a medical, electronically stored image on the silver halide light-sensitive hardcopy material disclosed hereinbefore comprises the steps of

- exposing said hardcopy material with a laser source within a time of less than or equal to 10 s for a size format of 14"x17"

25

- transporting said hardcopy material to an automatic processor within a time of less than or equal to 5 s
- processing dry-to-dry said hardcopy material in said automatic processor proceeding within a time of less than 50 s making use of developer and fixer solutions without hardener, and
- providing per minute at least 4 consecutive sheets with a size format of (43.2 x 35.6 cm) 17"x14" of the said silver halide light-sensitive hardcopy material of medical, electronically stored images.

30

5. Detailed description.

The hardcopy material used in this invention is particularly useful for the reproduction of electronically stored medical images by means of a laser recorder.

35 Said hardcopy material essentially is a silver halide photographic material comprising a support and at least one silver halide emulsion layer on one side of said support. Said at least one silver halide emulsion layer comprises cubic silver bromide or silver bromiodide crystals with an amount of at most 3 mole% of iodide. Preferably the silver halide emulsions have monodisperse silver bromide or silver bromiodide crystals. A monodisperse size distribution is obtained when 95% of the grains have a size that does not deviate more than 30% from the average grain size.

40 Cubic crystals are used as they allow rapid processing. In principle the same is possible with flat tabular crystals but, due to their heterogeneous silver halide grain distribution, their gradation is too low and due to the light-reflection of the developed silver which is situated at longer wavelengths the image tone is not neutral but shifted to a reddish brown colour.

45 The silver bromide or silver bromiodide emulsions used in accordance with this invention may be prepared by mixing the halide and silver salt solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide is preferably precipitated according to the double-jet method, in the presence of a colloid binder in a temperature controlled vessel provided with a solution inlet and stirring unit.

50 A preferred precipitation technique is the double-jet method, wherein the silver ion concentration is controlled during the precipitation and wherein the flow rate of the reacting solutions is enhanced as the precipitation proceeds, at such a rate that no renucleation appears. This method offers the possibility to get well-defined crystals having a regular cubic habit within a short precipitation time. Preferred cubic silverbromide or silver bromiodide crystals have a crystal size between 0.1 and 0.4 µm and even more preferably between 0.30 and 0.35 µm for reasons of image tone of the developed silver halide crystals. As a result a high covering power of the developed grains is obtained.

55 Colloidal binders used during the silver halide precipitation are hydrophilic binders such as the frequently used gelatin. Gelatin may, however, be replaced in part or integrally by synthetic, semi-synthetic, or natural polymers. Synthetic substitutes for gelatin are e.g. polyvinyl alcohol, poly-N-vinyl pyrrolidone, polyvinyl imidazole, polyvinyl pyrazole, polyacrylamide, polyacrylic acid, and derivatives thereof, in particular copolymers thereof. Natural substitutes for gelatin are e.g. other proteins such as zein, albumin and casein, cellulose, saccharides, starch, and alginates. In general, the

semi-synthetic substitutes for gelatin are modified natural products e.g. gelatin derivatives obtained by conversion of gelatin with alkylating or acylating agents, by grafting of polymerizable monomers on gelatin or prehardened gelatins with blocked functional groups as a consequence of this prehardening treatment, and cellulose derivatives such as hydroxyalkyl cellulose, carboxymethyl cellulose, phthaloyl cellulose, and cellulose sulphates.

5 The binder should of course dispose of an acceptably high number of functional groups, which by reaction with an appropriate hardening agent can provide a sufficiently resistant layer. Such functional groups are especially the amino groups, but also carboxylic groups, hydroxy groups, and active methylene groups.

Another substitute for gelatin may be silica as has been described in EP-Applications 392 092, 517 961 and EP 91202082.3 filed August 15, 1991 (corresponding to EP-A-0 528 476, published 24.2.93).

10 If gelatin is used as a binder gelatin may be lime-treated or acid-treated. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin may also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966). Preferably, use is made of photographically inert gelatin so as to add a reproducible amount of chemical sensitizers at the end of the precipitation or after flocculation or washing or redispersing the silver halide emulsion. To get a qualitatively good flocculate flocculating agents as e.g. polystyrene sulphonic acid etc. may be added before or after acidifying the emulsion. Other possibilities are offered by filtration techniques e.g. dialysis, ultrafiltration etc. so that the emulsion may be washed to a desired pAg value without the requirement to be redispersed afterwards. Emulsion flocculates need to be washed out by the addition of well-determined amounts of demineralized water, whether or not doped with small amounts of water-soluble salts.

20 The light-sensitive silver halide emulsion is preferably chemically sensitized as to reach its required sensitivity as described i.a. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature chemical sensitization may be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur e.g. thiosulphate, thiocyanate, thioureas, sulphites, mercapto compounds, and rhodamines. The emulsions may be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization may also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof may be used.

30 Preferably the silver halide crystals are predigested with weakly oxidizing compounds as e.g. thiosulphonic acids before being chemically ripened.

Chemical sensitization may occur in the presence of spectral sensitizers. The said spectral sensitizers have been chosen as a function of the laser source, showing a high light absorption at the exposure wavelength of the said laser source.

35 Spectral sensitizers may be added partially before, partially after or integrally after chemical sensitization with a total amount needed to reach the optimal coverage degree.

The light-sensitive silver halide emulsions may be spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that may be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes, rhodacyanine dyes.

40 In accordance with this invention rhodacyanine dyes are preferred with chemical structures as described e.g. in EP-Application 473 209.

45 Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, may have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A 2,933,390 and US-A 3,635,721, aromatic organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510, cadmium salts, and azaindene compounds.

50 The silver halide emulsion for use in accordance with the present invention may comprise compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof. Many known compounds may be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes,

tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB-A 1,203,757, GB-A 1,209,146, JA-Appl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphonic acid amide. Other compounds that may be used as fog-inhibiting compounds are metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chapitre VI.

Preferred stabilizers added to the emulsion in accordance with this invention are e.g. 4-hydroxy-6-methyl-1,3,3a, 7-tetraazaindene, 1-phenyl-5-mercaptotetrazole etc., thioether substituted 1-phenyl-5-mercaptotetrazoles as described in EP-Spec. 53 851 being more preferable, especially if they have a solubilizable group as those described in Research Disclosure No. 24236 (1984).

The fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the ripening thereof and mixtures of two or more of these compounds may be used.

A mixture of two or more silver halide emulsions having the same or different crystal sizes, a different or the same chemical ripening treatment and a different or the same coverage degree with one or more equal or different spectral sensitizers as described before may be added to at least one silver halide emulsion layer.

If more than one emulsion layer is coated onto one side of the support the same or different emulsions or emulsion mixtures may be present in the different layers. If the same emulsion or emulsion mixture is present in different emulsion layers it is a preferred embodiment to add distinct amounts of spectral sensitizer during chemical ripening and/or preparation for coating so as to get a broader exposure latitude for the material according to the invention and less sensitometric fluctuations in the processing of the hardcopy material.

For the material in accordance with this invention a total amount of coated silver halide crystals, expressed as the equivalent amount of silver nitrate, is preferably less than 6 g/m², so as to enable the unexposed silver halide crystals to be fixed entirely in the fixation step of the rapid processing cycle. Especially the presence of the preferred homogeneous cubic crystals described hereinbefore enables the customer to reach the desired sensitometry (high gradation and high maximum density) within short processing times with such a low coating amount of silver. Besides the said crystals ensure the preferred black image tone.

Other ingredients added to the emulsion layer(s), to an antihalation undercoat layer and/or to an antistress layer and/or to one or more backing layers are antihalation dyes, developing accelerators, plasticizers, hardeners, matting agents, thickening agents, surface active agents, polymers, antistatic agents, lubricants etc.

Antihalation dyes are chosen as a function of the applied laser source. Preferred antihalation dyes in accordance with this invention are red light absorbing dyes. At least one antihalation dye is preferably added to at least one emulsion layer in amounts necessary to reduce light scattering phenomena leading to a better sharpness. Preferably antihalation dyes are added in variable amounts during coating so as to adjust the sensitivity of the material. So it may be advantageous to introduce the antihalation dye or dyes by means of a dosing feeder just before coating to adjust the sensitivity of the photographic material as required by the product specifications. The said antihalation dye or dyes may be present in the form of solutions thereof, in the form of a gelatinous dispersion or in a solid particle state.

In accordance with this invention the same or different or a mixture of different developing accelerators may be added to at least one of the hydrophilic layers at the emulsion side. More preferably at least one development accelerator is added to at least one of the protective layers, preferably to the topcoat layer.

Development acceleration may be accomplished with the aid of various compounds, as disclosed in Research Disclosure No. 308119, December 1989, Chapter XXI, preferably polyoxyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805 - 4,038,075 - 4,292,400.

Especially preferred developing accelerators are polyoxyethylenes containing recurrent thioether groups as described in DE 2 360 878.

The photographic element used according to the present invention may further comprise various other additives such as e.g. compounds improving the dimensional stability of the photographic element, UV-absorbers, spacing agents, hardeners, and plasticizers.

Plasticizers suitable for incorporation in the emulsions according to the present invention are e.g. glycol, glycerine, or the latexes of neutral film forming polymers including polyvinylacetate, acrylates and methacrylates of lower alkanols, e.g. polyethylacrylate and polybutylmethacrylate.

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

Suitable UV-absorbers may be i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds

as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 μm . Spacing agents may be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents may be made i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US-A 4,614,708.

Matting agents used in the material in accordance with this invention are polymethylmethacrylate and/or silicon dioxide particles with a particle size diameter from 0.01 to 5 μm that are added to protective topcoat layer and more preferably from 0.025 to 2 μm .

Prior to coating any thickening agent may be used so as to regulate the viscosity of the coating solution, provided that they do not particularly affect the photographic characteristics of the silver halide light-sensitive photographic material. Preferred thickening agents include aqueous polymers such as polystyrene sulphonic acid, dextran, sulphuric acid esters, polysaccharides, polymers having a sulphonic acid group, a carboxylic acid group or a phosphoric acid group as well as colloidal silicas.

Polymeric thickeners well-known from the literature resulting in thickening of the coating solution may be used independently or in combination, even with colloidal silicas. Amounts may be suitably selected according to the kinds of silver halide and the kinds of layers or compounds to which these thickening agents are to be added. Patents concerning thickening agents are U.S. Patent No. 3,167,410, Belgian Patent No. 558,143 and JP OPI Nos. 53-18687 and 58-36768. Negative effects on physical stability possibly resulting from the addition of polymeric compounds can be avoided by exclusion of those compounds and restricting extra additions of colloidal silica.

The emulsions prepared and coated in the photographic material for use in accordance with the present invention are particularly advantageous for the formation of very thin emulsion layers, e.g. layers with a layer thickness of less than 5 μm , containing less than 5 g of gelatin, preferably about 3 g/m^2 . Such thin coated layers offer the advantage that besides the rapid processing applicability and the rapid drying of the wet processed material an improvement in sharpness is observed.

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

Since the drying characteristics in the processor are mainly determined by the water adsorption of the hydrophilic layers of the photographic material, and since the water adsorption is directly proportional to the gelatin content of the layers and inversely proportional to the amount of hardener, added to the layer, its composition is optimized with a low gelatin content and a high hardening degree so as to attain the object of this invention to allow hardener free processing within 50 seconds dry-to-dry cycle time.

In a preferred embodiment, a total amount of gelatin of less than 3 g/m^2 per side is present.

Hardeners may be added to the antistress layer before or during the coating procedure. The binders of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1-3-vinylsulphonyl-2-propanol, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxchloric acid. These hardeners can be used alone or in combination. The binders can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts.

Preferred hardening agents in accordance with this invention are formaldehyd and phloroglucinol, added respectively to the protective layer(s) and to the emulsion layer(s).

In accordance with this invention a hardening degree corresponding with a water absorption of the unexposed material of less than 8 g/m^2 after immersion in demineralized water at 24°C during 10 minutes is employed.

Backing layers applied to the material having at least one emulsion layer at one side of the hardcopy material used

in accordance with this invention essentially contain hydrophilic colloids, one or more antihalation dye(s), matting agent (s), surfactant(s), antistatic agent(s), lubricant(s) and hardening agent(s).

A common support of the photographic silver halide emulsion material in accordance with this invention may be a hydrophobic resin support.

5 Hydrophobic resin supports are well known to those skilled in the art and are made e.g. of polyester, polystyrene, polyvinyl chloride, polycarbonate, preference being given to polyethylene terephthalate.

The hydrophobic resin support may be provided with one or more subbing layers known to those skilled in the art for adhering thereto a hydrophilic colloid layer. Suitable subbing layers for polyethylene terephthalate supports are described e.g. in US-P 3,397,988, 3,649,336, 4,123,278 and 4,478,907.

10 Coating of the different layers of the photographic element may occur according to any of the known techniques for applying photographic coatings. In particular modern slide hopper and especially curtain coating techniques are applied. In order to increase the coating speed and/or to reduce the coating thickness when using curtain coating, polyacrylamides which are known to increase the shear viscosity can be added to the coating composition of the emulsion layer and/or protective antistress layer. Suitable polyacrylamides are copoly(acrylamide-(meth)acrylic acid) 15 e.g. COPOLY(acrylamide-acrylic acid-sodium acrylate) (87.5:4.1:8.4) in particular the commercial products ROHA-FLOC SF710 and ROHAFLOC SF 580 from ROHM. These polyacrylamides are preferably used in amounts of 10 to 500 ppm in the coating composition of the antistress layer and coating occurs simultaneously with the emulsion layer by curtain coating. In this way the emulsion layer thickness can be reduced and coating can occur at increased speed.

20 As it is a further object of this invention to have the disposal of a convenient imaging system wherein the silver halide light-sensitive hardcopy material of a medical, electronically stored image, perfectly fits, the said convenient imaging system in accordance with this invention is characterized by the following consecutive handling steps of the hardcopy material described hereinbefore:

- introduction of the said hardcopy material having format sizes of 35.6 x 43.2 cm (14"x17") in an exposure station
- 25 - exposure of said hardcopy material with a laser source within a time of less than or equal to 10 s
- transport of said hardcopy material to an automatic processing station within a time of less than 5 s
- processing dry-to-dry of said hardcopy material in said automatic processor within a time of less than 50 s, making use of developer and fixer solutions without hardener.

30 In these conditions the imaging system provides at least 4 consecutive sheets per minute of a silver halide light-sensitive hardcopy material of medical, electronically stored images.

A short exposure time with a laser source, taking less than or equal to 10 seconds for the said film format size for the hardcopy material is necessary to reach the objectives of this invention.

Suitable lasers may be gas lasers or solid state lasers. As a suitable gas laser a helium/neon gas laser is preferred.

35 As a preferred laser imager fulfilling the mentioned advantages we refer to the laser imager MATRIX LR 3300, trade name product marketed by Agfa-Gevaert.

The processing dry-to-dry within a time of less than 50 seconds of the hardcopy material in accordance with this invention is made possible by the steps of

- 40 - developing said hardcopy material in a developer without hardening agent
- fixing said hardcopy material in a fixer without hardening agent
- rinsing and drying the said hardcopy material.

45 Thanks to the special composition of the hardcopy material having a high degree of hardening as reflected by the reduced amount of water absorption disclosed hereinbefore, it is possible to make use of the said hardener free processing solutions. Developers and fixers useful in the processing cycle of the hardcopy material in accordance with this invention have been described in EP-Application No. 91202953.5, filed November 14, 1991 (corresponding to EP-A-0 542 354, published 19.5.93), although the compositions of the developers and fixers are not restricted thereto.

50 A particularly suitable developer solution for use in developing the hardcopy material within the scope of this invention is a developer which comprises an amount of less than 65 g of potassium sulphite per liter so as to reduce the smell of the developer to an acceptable level.

Analogously a suitable fixer solution for use in fixing the hardcopy material within the scope of this invention is a fixer which comprises an amount of less than 25 g of potassium sulphite per liter without the presence of acetic acid and wherein said fixer has a pH value of at least 4.5, again so as to make the fixer solution quasi odourless.

55 Besides it has to be recommended to regenerate the developer solution and the fixer solution for use in the processing of the hardcopy material according to this invention with concentrates of developer solutions and fixer solutions. In these circumstances, no dilution and mixing procedures are required before the regeneration bottles are adjusted to the processing unit.

Although it is possible to use whatever a processing unit adapted to the requirements described hereinbefore to reach the objectives concerning a perfect link between rapid processing and ecology, the objects of this invention concerning processing have e.g. been realized in the processing unit CURIX HT 530, trade name product marketed by Agfa-Gevaert.

Especially if the said laser imager MATRIX LR 3300 is linked with the CURIX HT 330 processing unit, on top of it, as has e.g. be realized in the laser imager processor MATRIX LR 3300P Laser Imager Processor, trade name product marketed by Agfa-Gevaert, the objectives of this invention can be fully realized. CURIX 330 again is a trade name product marketed by Agfa-Gevaert.

It is clear that within the scope of this invention any combination of a laser imager and a processing unit fulfilling the respective requirements for both of them in accordance with this invention may be used and is not limited to the laser imagers and processors described hereinbefore.

6. Examples.

Example No. 1 (comparative example)

A monodisperse negative working 100% silverbromide emulsion of cubic crystal structure having an average diameter of 0.35 μm was prepared by means of the double-jet technique with pAg-control. After flocculation, washing and redispersion said emulsion was chemically sensitized with optimum amounts of sulphur and gold compounds to reach the best possible fog-sensitivity relationship.

The emulsion was divided into three parts, called respectively part A, B and C. To each of these parts, inert gelatin was added in amounts to reach ratio values of gelatin to silver halide, the silver halide expressed as the equivalent amount of silver nitrate, of 0.4, 0.6 and 0.8 for the parts A, B and C respectively. Before coating the following ingredients were added per mole of silver halide:

1700 mg of linear trinuclear cyanine 2-1- β -phenyl-benzthiazol-N-ethyl-rhodanine-N-allyl-thiazole-4-phenyl-5-N-ethyl as spectral sensitizer,

740 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene as antifogging agent and stabilizer,

70 mg of 1-m-(carboxymethylthioacetamido)-phenyl-5-mercaptotetrazole as antifogging agent and stabilizer,

94 mg of phloroglucin as hardening accelerator

85 mg of polyethylacrylate as a plasticizer

Demineralized water was added so as to reach a concentration corresponding to 100 g of silver nitrate pro liter of coating solution.

A protective coating composition was prepared containing per liter the following ingredients in demineralized water:

- 42 g of an inert gelatin
- 20 g of an aqueous dispersion of matting agent with a particle size diameter of 2 μm comprising 3.2% of polymethylmethacrylate and 10% of gelatin
- 6.7 g of SYTON X30, trade name product from MONSANTO (silicium dioxide with an average diameter of 0.025 μm)
- 225 mg of chromium acetate as a hardening agent
- 300 mg of ammoniumperfluoro-octanoate (FC143, trade name product from 3M) and 750 mg of N-polyoxyethylene-N-ethyl-perfluoro-octane-sulfonamide (FC170C, trade name product from 3M) as surfactants
- 1500 mg of phenol as preserving agent
- 1000 mg of Mobilcer Q from MOBIL OIL as a lubricant An amount of formaldehyd was added as listed in the table below.

Both the emulsion layer and the antistress layer were coated simultaneously at one side onto a substrated 175 μm thick polyethylene terephthalate support. The emulsion layer was coated at a concentration of silver halide corresponding to 4.8 g of silver nitrate per m^2 , the protective layer at 1 g of gelatin/ m^2 . Due to the high amount the hardening agent should be added to the coating composition of the protective topcoat layer just before coating.

On the opposite side a conventional antihalation backing layer was coated.

After coating and drying, the coated materials were exposed with a He-Ne laser as a light source in a sensitometer with an exposure time of 90 ns per pixel. The processing was performed in a 90 seconds dry-to-dry cycle with conventional hardening X-ray chemicals (developer G138, trade name product of Agfa-Gevaert; fixer G 334, trade name product of Agfa-Gevaert). It is clear that it is not the normal procedure to process forehardened films in hardener containing processing solutions. In this example it has only been performed so for comparative purposes.

In Table 1 sensitometric data as well as amounts of water absorption (expressed in g/m^2) are summarized for the

EP 0 610 608 B1

emulsions A, B and C, coated with different amounts of gelatin per m² and hardened with varying amounts of formaldehyde expressed in g added per liter of the protective layer coating solution.

The sensitivity was determined at a density of 1; the gradation between densities 1.8 and 2.4 above fog and support density. The amount of water absorption, expressed in g/m² was determined as follows:

5

- preserving the dry film for 15 minutes in a conditioning room at 20°C and 30 % RH,
- covering the backing topcoat layer of the dry film with a water impermeable tape,
- weighing the dry film,
- immersing the unexposed material in demineralised water of 24°C for 10 minutes,
- 10 - sucking up the excessive amount of water present on top of the outermost layers and
- immediately determining the weight of the wet film and
- calculating the measured weight differences between the wet and the dry film per square meter.

This procedure was followed 2 weeks after coating to allow the materials to be hardened to a constant level.

15

As the amount of light needed to reach a density of 1.00 above fog and support density is lower for the more light-sensitive materials the sensitivity is higher for lower values, log exposure values given in table 1.

Table 1.

20

Sensitometric results and water absorption for hardcopy materials with a different degree of hardening and different amounts of gelatin coated /m ² .							
Sample		Gelatin/m ²	Formaldehyd	Sensitivity	Gradation	Water Abs.	
No.	Em.	(Em. + Antistr.)	(g/l antistr.)			(g/m ²)	
25	1	A	2.92	4	1.12	3.62	8.82
	2	A	2.9	7	1.14	3.54	7.18
	3	A	2.92	10	1.16	3.32	6.35
	4	B	3.88	4	1.12	3.49	10.40
	5	B	3.88	7	1.13	3.36	9.74
30	6	B	3.88	10	1.15	3.20	8.23
	7	C	4.84	4	1.13	3.30	13.04
	8	C	4.84	7	1.15	3.18	12.88
	9	C	4.84	10	1.15	3.09	12.01

35

From Table 1 it can be seen that the amount of water absorption is only reduced to a value of less than 8 g/m² for low coating amounts of gelatin and for a high degree of hardening as can be seen from samples No. 2 and 3. In 90 seconds processing all the samples give satisfying results as in that case also the drying time is longer than in more rapid processing conditions.

40

Example No. 2 (invention)

Samples No. 1, 2 and 3 from example No. 1 were processed after exposure in a dry-to-dry processing cycle of 45" with a one-part chemistry developer and fixer without hardening agents. The composition of said developer and fixer is given hereinafter.

45

Composition of the developer:

- concentrated part :

50

55

EP 0 610 608 B1

	water	200 ml
5	potassium bromide	6 grams
	potassium sulphite (65% solution)	247 grams
	ethylenediaminetetraacetic acid, sodium salt, trihydrate	9.6 grams
10		
	hydroquinone	112 grams
15	5-methylbenzotriazole	0.076 grams
	1-phenyl-5-mercaptotetrazole	0.040 grams
	sodium tetraborate (decahydrate)	18 grams
	potassium carbonate	50 grams
20	potassium hydroxide	57 grams
	diethylene glycol	100 grams
	potassium iodide	0.088 grams
25	4-hydroxymethyl-4methyl-1-phenyl- 3-pyrazolidinone:	12 grams
	Water to make 1 liter	

pH adjusted to 11.15 at 25°C with potassium hydroxide.

For initiation of the processing one part of the concentrated developer was mixed with 3 parts of water.

30 No starter was added.

The pH of this mixture was 10.30 at 25°C.

Composition of the fixer:

35 - concentrated part :

sodium thiosulfate decahydrate	628 grams
sodium sulphite	40 grams
boric acid	36 grams
citric acid monohydrate	40 grams
water to make 1 liter	

45 pH adjusted with sodium hydroxyde to 6.60 at 25°C

To make this fixer ready for use one part of this concentrate was mixed with 1 part of water. A pH of 6.78 was measured at 25°C.

The processing machine was the CURIX HT 330, trade name product marketed by Agfa-Gevaert, with the following time (in seconds) and temperature (in °C) characteristics:

50	loading	: 0.3 s	
	developing	: 10.0 s	35°C in the developer described
	hereinbefore		
55	cross-over	: 3.0 s	
	fixing	: 10.0 s	35°C in the fixer described
	hereinbefore		

cross-over : 3.0 s
 rinsing : 6.6 s
 cross-over : 2.6 s
 drying : 9.9 s

 total 45.4 s

Since shorter development times in the hardener-free developer and fixer solutions described hereinbefore lead to unacceptable low gradations three additional samples (No. 10, 11 and 12, see table 2) were made having the same compositions as the samples No. 1, 2 and 3 respectively of Table 1 except that 2.5 ml of an aqueous solution of the copolymer of epichlorhydrine-mono glyceryl-thiomethylethylene oxide were added as development accelerator to the coating composition of the protective layers.

Table 2 shows that this development accelerator is compensating very well for the loss in gradation due to shorter development times. It is clearly illustrated in the last column of Table 2 that the samples with the lowest water absorption are drying very well in the hardener-free rapid processing cycle. Said last column contains figures that are indicative for a better drying quality as the figures are lower.

A "*" -sign indicates that even in extreme drying situations it was not possible to get a good drying quality for the sample.

Table 2.

Sensitometric results and drying quality for materials with a different degree of hardening.						
Sample		Development Accelerator	Formaldehyd	Sensitivity	Gradation	Drying quality
No.	Em.		(g/l antistress)			
1	A	-	4	1.15	3.03	*
2	A	-	7	1.16	2.95	8
3	A	-	10	1.18	2.81	2
10	A	2.5	4	1.12	3.60	*
11	A	2.5	7	1.10	3.54	9
12	A	2.5	10	1.10	3.41	2

(Samples 1 and 10 are comparative tests not in accordance with the invention)

Claims

- Method of reproducing an electronically stored medical image on a hardcopy material for medical hardcopy obtained by means of a laser recorder, wherein said hardcopy material comprises a support and on only one side thereof at least one silver halide emulsion layer and at least one hydrophilic colloid layer, wherein said material has a hardening degree corresponding with a water absorption of less than or equal to 8 g/m² at the emulsion side, the said water absorption being measured as defined herein, and wherein said silver halide emulsion essentially consists of homogeneous cubic silver bromide or silverbromiodide crystals with at most 3 mole% of iodide ions. said method comprising the steps of
 - exposing said hardcopy material with a laser source within a time of less than or equal to 10 s for a size format of 35.6 x 43.2 cm (14"x17")
 - transporting said hardcopy material to an automatic processor within a time of less than or equal to 5 s
 - processing dry-to-dry said hardcopy material in said automatic processor proceeding within a time of less than 50 s making use of developer and fixer solutions without hardener.
 - providing per minute at least 4 consecutive sheets with a size format of 35.6 x 43.2 cm (17"x14").
- Method according to claim 1, wherein said hardcopy material comprises homogeneous cubic silver bromide or silver bromiodide crystals having an average crystal diameter between 0.1 and 0.4 µm.
- Method according to claim 1 or 2, wherein the total gelatin content at the emulsion side is less than or equal to 3

g/m² and the silver content at the emulsion side, expressed as the equivalent amount of silver nitrate, is less than 5 g/m².

4. Method according to any of claims 1 to 3, wherein said silver halide photographic material comprises in at least one hydrophilic colloid layer at the emulsion side at least one development accelerator.
5. Method according to claim 4, wherein development accelerator is a polyoxyethylene polymer having recurrent thioether groups.

Patentansprüche

1. Verfahren zur Reproduktion eines elektronisch gespeicherten, medizinischen Bildes auf einem medizinischen Hartkopiematerial zur Wiedergabe eines laseraufgezeichneten medizinischen Bildes, dadurch gekennzeichnet, daß das Hartkopiematerial einen Träger und auf einer Trägerseite wenigstens eine Silberhalogenidemulsionsschicht und wenigstens eine hydrophile Kolloidschicht enthält, wobei der Härungsgrad des Materials einer Wasserabsorption von weniger als oder gleich 8 g/m² auf der Emulsionsseite entspricht, die Wasserabsorption wie in dieser Patentschrift beschrieben gemessen wird und die Silberhalogenidemulsion hauptsächlich aus homogenen kubischen Silberbromid- oder Silberbromiodidkristallen mit höchstens 3 Mol-% Iodidionen besteht, wobei dieses Verfahren die folgenden Stufen umfaßt :

- die Belichtung des Hartkopiematerials mit einer Laserquelle innerhalb einer Zeit von weniger als oder gleich 10 s für ein Schnittformat von 35,6 x 43,2 cm
- den Transport des Hartkopiematerials zu einem automatischen Entwicklungsgerät innerhalb einer Zeit von weniger als oder gleich 5 s
- die Trocken/Trocken-Verarbeitung des Hartkopiematerials im automatischen Entwicklungsgerät innerhalb einer Zeit von weniger als 50 s, wobei Entwickler- und Fixierlösungen ohne Härtungsmittel eingesetzt werden, und
- das Herstellen, pro Minute, von wenigstens 4 aufeinanderfolgenden Bogen mit einem Schnittformat von 35,6 x 43,2 cm.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Hartkopiematerial homogene kubische Silberbromid- oder Silberbromiodidkristalle mit einem durchschnittlichen Kristalldurchmesser zwischen 0,1 und 0,4 µm enthält.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Gesamtgelatinegehalt auf der Emulsionsseite nicht mehr als 3 g/m³ beträgt und der als die äquivalente Silbernitratmenge ausgedrückte Silbergehalt auf der Emulsionsseite weniger als 5 g/m² beträgt.

4. Verfahren nach irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß das photographische Silberhalogenidmaterial in wenigstens einer hydrophilen Kolloidschicht auf der Emulsionsseite wenigstens einen Entwicklungsbeschleuniger enthält.

5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß der Entwicklungsbeschleuniger ein Polyoxyethylenpolymeres mit sich wiederholenden Thioethergruppen ist.

Revendications

1. Une méthode de reproduction d'une image médicale stockée électroniquement sur un matériau de copie tirée pour l'usage d'une copie tirée médicale au moyen d'une photocomposeuse laser, caractérisée en ce que ce matériau de copie tirée comprend un support et, seulement sur un côté de celui-ci, au moins une couche d'une émulsion à base d'halogénure d'argent et au moins une couche colloïdale hydrophile, caractérisée en ce que ce matériau possède un degré de durcissement correspondant à une absorption d'eau inférieure ou égale à 8 g/m² du côté de l'émulsion, l'absorption d'eau étant mesurée comme il est défini dans ce brevet, et caractérisée en ce que l'émulsion d'halogénure d'argent consiste essentiellement en des cristaux homogènes cubiques de bromure d'argent ou de bromo-iodure d'argent ayant maximum 3 moles % d'ions d'iode. Cette méthode comprend les phases suivantes:

EP 0 610 608 B1

- exposer ce matériau de copie tirée à une source laser durant au plus 10 secondes pour un format de 35,6 x 43,2 cm
 - transporter ce matériau de copie tirée vers un processeur automatique durant au plus 5 secondes
 - traiter d'une manière sec à sec le matériau de copie tirée dans ce processeur automatique durant un délai inférieur à 50 secondes, en utilisant des bains de développeur et de fixateur qui sont exempts d'un durcisseur
 - produire au moins 4 feuilles consécutives par minute d'un format de 35,6 x 43,2 cm.
- 5
- 10
- 15
- 20
- 25
- 30
- 35
- 40
- 45
- 50
- 55
2. Une méthode selon la revendication 1, caractérisée en ce que le matériau de copie tirée comprend des cristaux homogènes cubiques de bromure d'argent ou de bromo-iodure d'argent ayant un diamètre de cristal moyen entre 0,1 et 0,4 μm .
 3. Une méthode selon les revendications 1 ou 2, caractérisée en ce que la quantité totale de la gélatine du côté de l'émulsion est inférieure ou égale à 3 g/m^2 et la quantité de l'argent du côté de l'émulsion, exprimée comme la quantité équivalente du nitrate d'argent, est inférieure à 5 g/m^2 .
 4. Une méthode selon l'une quelconque des revendications 1 à 3, caractérisée en ce que le matériau photographique à base d'halogénure d'argent comprend au moins un accélérateur de développement dans au moins une couche colloïdale hydrophile du côté de l'émulsion.
 5. Une méthode selon la revendication 4, caractérisée en ce que l'accélérateur de développement est un polymère d'oxyde de polyéthylène ayant des unités récurrentes d'un thioéther.