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# (54) Method for preparing tabular grains rich in silver bromide in the presence of specific gelatines

(57) The present invention discloses a method for preparing an emulsion having grains rich in silver bromide in the presence of gelatin as a protective colloid, wherein at least 70 % of the total projected area of all grains is provided by tabular grains, said method comprising following steps :

- preparing in a reaction vessel a dispersion medium containing gelatin having less than 30 μmoles of methionine per gram,
- precipitating therein silver halide crystal nuclei by double-jet precipitation of an aqueous silver nitrate and an aqueous solution comprising halide ions, wherein less than 10 % by weight of the total amount of silver nitrate used is consumed,
- adding to said reaction vessel gelatin having 30 or more  $\mu moles$  of methionine per gram,
- growing said silver halide crystal nuclei by further precipitation of silver halide by means of double-jet precipitation of an aqueous silver nitrate solution and an aqueous solution comprising halide ions, wherein more than 90 % by weight of the total amount of silver nitrate is consumed, and wherein said tabular grains exhibit
- an average aspect ratio of at least 2:1 and more preferably from 5:1 to 15:1;
- an average thickness of more than 0.07 μm, preferably up to 0.20 μm;
- a coefficient of variation of the grain size distribution of tabular grains of less than 0.40.

By this method a silver halide emulsions rich in silver bromide is prepared, wherein at least 70 % of the total projected area of all grains is provided by tabular grains having grain characteristics as set forth above and wherein gelatin contains methionine in an average amount of from 25 to 42.5  $\mu$ moles per gram of said gelatin.

## Description

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- 1. Field of the invention.
- 5 This invention relates to a method for preparing silver halide grains rich in silver bromide in the presence of specific gelatines.

2. Background of the invention.

10 Tabular silver halide grains are grains possessing two parallel crystal faces with a ratio between diameter of a circle having the same area as these crystal faces, and thickness, being the distance between the two major faces, of two or more.

Tabular grains are known in the photographic art for quite some time. As early as 1961 Berry et al. described the preparation and growth of tabular silver bromoiodide grains in Photographic Science and Engineering, Vol 5, No 6. A discussion of tabular grains appeared in Duffin, Photographic Emulsion Chemistry, Focal Press, 1966, p. 66-72.

Early patent literature includes Bogg US-A 4,063,951, Lewis US-A 4,067,739 and Maternaghan US-A's 4,150,994; 4,184,877 and 4,184,878. However the tabular grains described herein cannot be regarded as showing a high diameter to thickness ratio, commonly termed aspect ratio. In a number of US-A's filed in 1981 and issued in 1984 tabular grains with high aspect ratio and their advantages in photographic applications are described as e.g. US-A's 4,434,226; 4,439,520; 4,425,425 and 4,425,426 and in Research Disclosure, Volume 225, Jan 1983, Item 22534.

- 20 4,439,520; 4,425,425 and 4,425,426 and in Research Disclosure, Volume 225, Jan 1983, Item 22534. For radiographic applications photographic advantages of tabular grains if compared with normal globular grains are a high covering power at high forehardening levels as set forth in US-A 4,414,304. Further a high developability and high sharpness especially in double side coated spectrally sensitised materials can be obtained. The thinner the tabular grains and the lower the number of non-tabular grains in the total grain population the greater these advantages. An
- 25 increased number of tabular grains rich in bromide in the total grain population is obtained if use is made in the preparation method of so-called "oxidised gelatin", characterised by the presence in the said gelatin of amounts of methionine of less than 30 µmoles per gram of gelatin as in US-A 4,713,320, corresponding with EP-A 0 228 256 and in Research Disclosure 29945, published March 1989. In EP-A 0 228 256 it has even been established that while it should be possible to use any conventional peptizer toward the end of precipitation with minimal adverse impact on the emulsions, it
- 30 is preferred that the low methionine gelatino-peptizer be used as a sole peptizer throughout the formation and growth of thin tabular grains. In the Examples related therewith emulsion grains having a thickness of up to 0.050 µm have been prepared, wherein a relatively large variation on thickness and on coefficients of variation have been shown.
- A preparation method of tabular grain emulsions wherein in the grain growth process use is made of gelatin derivatives with chemically modified NH<sub>2</sub>-groups and wherein said gelatin has a specific methionine content has been described in EP-A 0 697 618. Modification of the methionine content of a gelatinous dispersion medium by means of an oxidiser which should be added to the reaction vessel immediately before nucleation formation has been described in US-A 5,372,975, wherein seed grains are further added. Seed grains formed in the presence of an oxidising agent have been described in JP-A 05-210187, in JP-A 06-003758 and in JP-A 06-003759. Processing a gelatin solution by means of H<sub>2</sub>O<sub>2</sub> has been described in JP-A 05-341415. Other oxidising agents besides hydrogen peroxide as e.g. ozone, peroxy acid salts, halogens, thiosulphonic acid salts, guinones and organic peroxides have been used in US-A
- 5,489,504. Further in order to provide tabular grains having small twin-plane separations in tabular grains rich in silver bromide a preparation method making use of oxidised gelatin has been described in US-A 5,219,720.

As a high covering power offers the possibility to coat lower amounts of silver it is, also with respect to ecology, of utmost importance to prepare tabular grains rich in silver bromide having an enhanced covering power. It is however remarkable that, just when use is made of oxidised gelatin, wherein as set forth hereinbefore, a methionine content of less than 30 µmoles per gram of gelatin is present, the covering power is decreased for the same hardening degree of the layers wherein the emulsions containing tabular grains rich in silver bromide are coated. Moreover this is accompanied by a serious reduction in contrast.

## 50 OBJECTS OF THE INVENTION

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Therefore it is a first object of this invention to provide a method for preparing tabular grains rich in silver bromide having a thickness of at least 0.07 µm and an average aspect ratio of at least 2:1 having a covering power as high as possible for different hardening levels of the layer material wherein the said tabular grains are coated in gelatinous emulsion form.

A further object of this invention is to obtain tabular grains rich in silver bromide accounting for an amount by number of the total amount of grains as high as possible in order to have said tabular grains account for at least 70 % of the total projective area of all grains.

Other objects will become apparent from the description hereinafter.

## SUMMARY OF THE INVENTION

- In accordance with the present invention a method is provided for preparing an emulsion having grains rich in silver bromide in the presence of gelatin as a protective colloid, wherein at least 70 % of the total projected area of all grains is provided by tabular grains, said method comprising following steps :
  - preparing in a reaction vessel a dispersion medium containing gelatin having less than 30 μmoles of methionine per gram,
  - precipitating therein silver halide crystal nuclei by double-jet precipitation of an aqueous silver nitrate and an aqueous solution comprising halide ions, wherein less than 10 % by weight of the total amount of silver nitrate used is consumed,
  - adding to said reaction vessel gelatin having 30 or more μmoles of methionine per gram,
- 15 growing said silver halide crystal nuclei by further precipitation of silver halide by means of double-jet precipitation of an aqueous silver nitrate solution and an aqueous solution comprising halide ions, wherein more than 90 % by weight of the total amount of silver nitrate is consumed.

By this method a silver halide emulsion is prepared wherein said tabular grains further exhibit:

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- an average aspect ratio of at least 2:1 and more preferably from 5:1 to 15:1;
- an average thickness of more than 0.07 μm, more preferably up to 0.20 μm;
- a coefficient of variation of the grain size distribution of tabular grains of less than 0.40.
- 25 Moreover a gelatinous emulsion having silver bromide, silver bromoiodide or silver bromochloroiodide grains with the characteristics set forth above is provided wherein at least 70 % of the total projected area of all grains is provided by tabular grains having grain characteristics as set forth above and wherein gelatin contains methionine in an average amount of from 25 to 42.5 µmoles per gram of said gelatin.
- 30 DETAILED DESCRIPTION OF THE INVENTION

After preparing in a reaction vessel a dispersion medium containing gelatin having less than 30 µmoles of methionine per gram according to the method of this invention, a total amount of silver nitrate of less than 10 % by weight, and more preferably 0.5 % to 5.0 %, is added during the nucleation step which preferably consists of an approximately equimolecular simultaneous addition of silver nitrate and halide salts at a pBr of 1.0 to 2.0.

The rest of the silver nitrate and halide salts is added during one or more consecutive double jet growth step(s) after having added to said reaction vessel, according to the method of this invention, gelatin having 30 or more  $\mu$ moles of methionine per gram so that the total amount of gelatin contains per gram an average amount of from 25 to 42.5  $\mu$ moles of methionine.

40 Further, according to the method of the present invention, growing said silver halide crystal nuclei proceeds by precipitation of silver halide by means of double-jet precipitation of an aqueous silver nitrate solution and an aqueous solution comprising halide ions, wherein more than 90 % and more preferably up to 95 % by weight of the total amount of silver nitrate is consumed.

The different steps of the precipitation can be alternated by physical ripening steps or by so called "neutralisation steps", during which the pAg value is changed to a value required in the next growth stage by adding an amount of silver nitrate solution or a water soluble halide salt within a well-defined time of addition by means of the single-jet technique. Alternative ways to regulate the pAg to the desired value before continuing the processing are diluting the emulsion present in the reaction vessel, diafiltration or ultrafiltration and even flocculation and washing procedures, the last techniques being preferred to concentrate the emulsion crystals in the reaction vessel. Any combination or any choice of the mentioned techniques may be applied thereto.

At least two growth steps are commonly used. In the first growth step the crystal grows laterally and in the second growth step a simultaneous growth in the direction perpendicular to the main planes is induced. The ratio of the second growth step to the first growth step and the pBr in this second growth step is such that the tabular grains rich in silver bromide at the end of the preparation according to the method of the present invention exhibit an average aspect ratio

of at least 2:1, more preferably from 5:1 to 15:1, and wherein tabular grains rich in silver bromide in the presence of gelatin having a specific composition with respect to methionine content account for at least 70 %, and more preferably at least 90 % of the total projected area of all grains. Further said tabular grains rich in silver bromide, prepared according to the method of this invention have an average thickness of more than 0.07 μm, i.a. up to 0.30 μm, and more preferably

up to 0.20  $\mu$ m and a coefficient of variation of the grain size distribution of tabular grains of less than 0.40 and more preferably between 0.10 and 0.20. In order to obtain such a high degree of homogeneity useful compounds added to the reaction vessel are polyalkyleneoxides as in US-A's 5,252,442 and 5,147,771.

During the growth step(s) an increasing flow rate of silver and halide solutions is preferably applied, e.g. a linearly increasing flow rate. Typically the flow rate at the end is about 3 to 10 times greater then at the start of the growth step. For a succesful preparation of emulsions having tabular grains rich in silver bromide according to the method of the present invention the pBr before the start and during the different stages of the precipitation is maintained at a welldefined value as will become apparent from the examples hereinafter.

It is possible in the method of the present invention to prepare nuclei in a separate vessel and to grow the said nuclei in another vessel, the proviso that the gelatinous solutions in both vessels have a methionine content per gram of gelatin as set forth hereinbefore.

At the end of the precipitation, according to the method of this invention the reaction vessel thus contains gelatin having 30 or more µmoles of methionine per gram so that the total amount of gelatin contains per gram an average amount of from 25 to 42.5 µmoles of methionine. Further according to the method of this invention a ratio by weight of gelatin having less than 30 µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methionine per gram to gelatin having 30 or more µmoles of methion

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is from 1:5 to 1:50. A gelatinous emulsion having tabular grains rich in silver bromide is thus obtained, wherein in a preferred embodi-

ment said grains are composed of silver bromide, silver bromoiodide, silver bromochloride or silver bromochloroiodide grains, wherein at least 70 % of the total projected area of all grains is provided by said tabular grains having an average
 aspect ratio of at least 2:1 and a thickness of more than 0.07 μm and wherein gelatin contains methionine in an average amount of from 25 to 42.5 μmoles per gram of said gelatin.

In order to determine the methionine content of gelatin many references from literature are available as e.g. in J.Phot.Sc., Vol. 28(1980), p.111-118 wherein as most obvious reducing substances in gelatin methionine residues of the macromolecule are determined in reaction with Au(III)-ions. The so-called "gold number" permits determination of

- 25 amounts of methionine in the gelatin following the rule that 1 μmole of Au corresponds with 1.6 μmole of methionine. In J.Phot.Sc., Vol. 33(1989), p.10-17 the methionine content was determined using the gaschromatographic procedure developed by Apostolatos and Hoff (Anal. Biochem. Vol. 118(1981), p.126) and applied to gelatin by Rose and Kaplan. In this article calorimetry is used in a quantitative procedure for determining methionine (constant over initial pH range examined: 3.0 8.0). In J.Phot.Sc., Vol. 40(1992), p.149-151 amounts of methionine, methionine sulphoxide and
- 30 methionine sulphone are determined by a chromatographic technique for amino acids (Hitachi Amino Acid Analyser), whereas in J.Phot.Sc., Vol. 41(1993), p.172-175 these compounds are determined by HPLC. In J.Phot.Sc., Vol. 39(1995), p. 367-372 it has been established that a good correlation between methionine content determined by Rose and Kaplan making use of gas chromatographic techniques (4th IAG Conference, Fribourg 1985, Amman-Brass & Pouradier) and the Scatchard technique (described in J.Phot.Sc., Vol. 42(1994), p.117-119) can be found. In the said
- 35 technique the interaction at pH = 3.0 of Ag<sup>+</sup> and gelatin is determined by means of potential measurements of free Ag<sup>+</sup>ions.

Preferably according to the method of this invention in said silver bromiodide or silver bromochloroiodide iodide is present in an amount of up to 3 mole % and in a preferred embodiment iodide is provided by means of an iodide releasing agent. Patent applications referring to methods wherein iodide releasing agents are used are e.g. EP-A's 0 563 701,

- 40 0 563 708, 0 561 415 and 0 651 284. Preparation of silver bromoiodide emulsion crystals can be achieved by mixing a soluble bromide and a soluble iodide salt in one or more of the halide solutions up to the desired mole % concentrations required in each preparation step or by a triple jet technique, or separate addition of an iodide containing aqueous solution. Due to the lower solubility of silver iodide in comparison with silver bromide, said iodide ions are able to displace bromide ions from the grain, a technique known in the art as conversion. lodide ions may also be incorporated into the
- 45 silver halide crystal lattice by the addition of a previously prepared silver iodide micrate emulsion, composed of either pure silver iodide or mixed halides, but as already set forth hereinbefore in a preferred embodiment iodide releasing agents are used, at least partially, e.g. in one or more conversion steps during or at the end of the precipitation. Even bromide releasing agents are not excluded in the precipitation steps according to the method of this invention.

Silver chloride, if present as in silver bromochloride or silver bromochloriodide emulsions, takes about up to 20 mole % in the composition of the silver halide grains rich in silver bromide.

Two or more types of tabular silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in accordance with the present invention.

The size distribution of the tabular silver halide particles of the photographic emulsions to be used according to the present invention can be monodisperse or heterodisperse as already set forth hereinbefore. The tabular grain emulsion becomes more heterodisperse by adding more silver nitrate during growing of the nuclei prepared in the nucleation step

at a pBr value lower than 1.7. A more heterodisperse distribution is even obtained for a pBr value lower than 1.2.

In this way low contrast heterodisperse emulsions with a coefficient of variation of the tabular grains between 0.20-0.40, and even between 0.30-0.40. In applications wherein higher contrast is preferred, more homodisperse emulsions are preferred with coefficients of variation between 0.10 and 0.20.

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After completion of the precipitation a wash technique in order to remove the excess of soluble salts may be applied at a pH value which can vary during washing. If in that case the emulsion is washed by diafiltration by means of a semipermeable membrane. This technique is also called ultrafiltration. Such procedures are disclosed e.g. in Research Dis-

5 closure Vol. 102, Oct. 1972, Item 10208, Research Disclosure Vol. 131, March, Item 13122 and Mignot US Patent 4,334,012. Preferably, at the start of the ultrafiltration, pH and pAg are the same as at the end of the precipitation without any adjustment.

Besides these previously mentioned dialysis techniques like ultrafiltration flocculation by polymeric reagents at a pH value below 4.0, followed by washing and redispersion may be applied. Emulsion washing has e.g. described in Research Disclosure N° 36544 (1994), Chapter III.

Tabular silver halide emulsions rich in silver bromide prepared by the method of the present invention can be chemically sensitised as described e.g. 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 Ver-

- 15 lagsgesellschaft (1968). Chemical sensitisation has e.g. also been described in Research Disclosure N° 36544 (1994), Chapter IV. As described in said literature chemical sensitisation can 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. Said compounds containing sulphur can also be, at least partially, replaced by compounds containing selenium and/or tellurium. The emulsions may be sensitised also by means of gold-sulphur, gold-
- 20 sulphur-selenium, gold-selenium ripeners or by means of reductors e.g. tin compounds as described in GB Patent 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. The tabular silver halide emulsions may be spectrally sensitised with methine dyes such as those described by F.M.

Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons and in Research Disclosure N° 36544 (1994), Chapter V. Dyes that can be used for the purpose of spectral sensitisation include cyanine dyes, mero-

- 25 cyanine dyes, complex cyanine dyes, complex merocyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes and complex merocyanine dyes. A survey of useful chemical classes of spectral sensitizing dyes and specific useful examples in connection with tabular grains is given in the already cited Research Disclosure Item 22534. Oxacarbocyanines have been described e.g. in US-P 5,434,042. Especially preferred green sensitisers in connection with the present invention are anhydro-5,5'-
- 30 dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide and anhydro-5,5'-dichloro-3,3'-bis(n.sulfopropyl)-9ethyl-oxa-carbo-cyanine hydroxide. Imidacarbocyanines as e.g. those described in Research Disclosure N° 37312 (1995) may be useful as well as combinations of oxacarbocyanines and imidacarbocyanines as in EP-A 0 590 593 from the viewpoint of sensitivity as well as from the viewpoint of decolouring properties and stain removal in the processing of materials containing spectrally sensitised tabular grains rich in silver bromide as in this invention.
- In classical emulsion preparation spectral sensitisation traditionally follows the completion of chemical sensitisation. However, in connection with tabular grains, it is specifically considered that spectral sensitisation may occur simultaneously with or may even precede completely the chemical sensitisation step: the chemical sensitisation after spectral sensitisation is believed to occur at one or more ordered discrete sites of tabular grains. This may also be done with the emulsions prepared according to the present invention, wherein the chemical sensitisation proceeds in the
- 40 presence of one or more phenidone and derivatives, a dihydroxy benzene as hydroquinone, resorcinol, catechol and/or a derivative(s) therefrom, one or more stabiliser(s) or antifoggant(s), one or more spectral sensitiser(s) or combinations of said ingredients. Especially 1-p-carboxyphenyl, 4,4' dimethyl-pyrazolidine-3-one may be added as a preferred auxiliary agent.
- The gelatinous silver halide emulsion rich in silver bromide of the present invention, characterised by a specific gel-45 atin composition as set forth hereinbefore is further coated in hydrophilic layer(s) which may, just as non-light-sensitive layers of the photographic material according to this invention, comprise compounds preventing the formation of fog or stabilising the photographic characteristics during the production or storage of the photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabiliser to the silver halide emulsion layer or to other coating layers in water-permeable relationship therewith such as an undercoat or a
- 50 protective layer. Suitable examples are e.g. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and penta-
- 55 zaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB 1,203,757, GB 1,209,146, JA-Appl. 75-39537, and GB 1,500,278, and 7-hydroxy-s-triazolo-[1,5a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid and benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds

are metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure Nº 17643 (1978), Chapter VI and in RD Nº 36544 (1994), Chapter VII. Many of these fog-inhibiting compounds may have been already added during the chemical ripening of the tabular silver halide crystals rich in silver bromide. It is clear that additional gelatin is added in a later stage of the emulsion preparation, e.g. after washing, to establish optimal coating con-

- ditions and/or to establish the required thickness of the coated emulsion layer. Preferably a gelatin to silver halide ratio 5 ranging from 0.3 to 1.0 is then obtained, wherein extra gelatin added is not required to have a compostion as specific as in the preparation step of the grains according to the method of the present invention. Another binder may also be added instead of or in addition to gelatin. Useful vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda have been described e.g. in Research Disclosure N° 36544 (1994), Chapter II.
- 10 The gelatin binder of the photographic material having at least one gelatinous emulsion according to the present invention can be forehardened 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-
- 15 triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US-A 4,063,952 and with the onium compounds as disclosed in EP-A 0 408 143.
- The gelatinous emulsions comprising tabular grains rich in silver bromide of the present invention can be used in various types of photographic elements, e.g. black and white silver halide photographic materials, like materials used 20 for X-ray diagnostic purposes, or colour sensitive materials.

In a preferred embodiment according to the present invention said photographic element or material comprises a support and on one or on each side thereof one or more silver halide emulsion layer(s) coated from a gelatinous emulsion according to this invention. More specifically said photographic material is a single-side or double-side coated Xray material.

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The single-side coated X-ray material may contain one single emulsion layer, as it is the case for many applications, or it can be built up by two or even more emulsion layers. In X-ray photography a material with a single or a duplitized emulsion layer coated on one or both sides of the support thus contains at least one gelatinous silver halide emulsion according to the invention. By using duplitized emulsions differing in photographic speed by at least 0.15 log E a gain

30 in cross-over exposure in double side coated materials can be obtained. In the case of colour photography the material contains blue, green and red sensitive layers each of which can be single coated, but merely consist of double or even triple layers. Besides the light sensitive emulsion layer(s) the photographic material may contain several light-insensitive layers, e.g. a protective layer, one or more backing layers, one or more subbing layers, one or more intermediate layers e.g. filter layers and even an afterlayer containing e.g. the hardening agent(s), the antistatic agent(s), filter dyes for 35 safety-light purposes etc.

The photographic element of the present invention may further comprise various kinds of coating physical property modifying addenda as described in RD N° 36544 (1994), Chapter IX, wherein coating aids, plasticizers and lubricants, antistats and matting agents have been described. Development acceleration can be accomplished by incorporating in the emulsion layer or adjacent layers various compounds, preferably polyalkylene derivatives having a molecular weight

of at least 400 such as those described in e.g. US-A's 3,038,805; 4,038,075 and 4,292,400 as well as in EP-A's 0 634 40 688 and 0 674 215.

The photographic element of 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 and plasticizers.

- Suitable additives for improving the dimensional stability of the photographic element are e.g. dispersions of a 45 water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl(meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.
- Suitable UV-absorbers are e.g. aryl-substituted benzotriazole compounds as described in US Patent 3,533,794, 4-50 thiazolidone compounds as described in US Patent 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US Patents 3,705,805 and 3,707,375, butadiene compounds as described in US Patent 4,045,229, and benzoxazole compounds as described in US Patent 3,700,455 and those described in RD N° 36544 (1994), Chapter VI, wherein also suitable optical brighteners are mentioned. UV-
- absorbers are especially useful in colour materials where they prevent the fading by light of the colour images formed 55 after processing.

Spacing agents can be present of which, in general, the average particle size is comprised between 0.2 and 10 µm. Spacing agents can 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 can be made e.g. 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 Patent 4,614,708.

- 5 The photographic material can contain several non-light sensitive layers, e.g. an antistress topcoat layer, one or more backing layers, and one or more intermediate layers eventually containing filter- or antihalation dyes that absorb scattering light and thus promote the image sharpness. Suitable light-absorbing dyes used in these intermediate layers are described in e.g. US Patents 4,092,168, US 4,311,787, DE 2,453,217, and GB Patent 7,907,440. Situated in such an intermediate layer between the emulsion layers and the support there will be only a small negligable loss in sensi-
- 10 tivity but in rapid processing conditions decolouration of the filter dye layers may form a problem. Therefor it should be recommended to decrease the thickness of the whole coated layer packet resulting in shorter drying times after washing in the processing cycle. Alternatively the use of intermediate layers situated between emulsion layer(s) and support, reflecting the fluorescent light emitted by the screens may bring a solution. As the light emitted from the screens by the phosphors incorporated therein is a very important source of light-scattering the addition of appropriate filter dyes to the
- 15 screens may be recommended. In the presence in the screens of e.g. green light-emitting phosphors use may be made of specific dyes as MAKROLEX ORANGE G or GG, trademarked products of BAYER AG. One or more backing layers can be provided at the non-light sensitive side of the support of materials coated with

at least one emulsion layer at only one side of the support. These layers which can serve as anti-curl layer can contain e.g. matting agents like silica particles, lubricants, antistatic agents, light absorbing dyes, opacifying agents, e.g. titanium oxide and the usual ingredients like hardeners and wetting agents.

The support of the photographic material may be opaque or transparent, e.g. a paper support or resin support. When a paper support is used preference is given to one coated at one or both sides with an Alpha-olefin polymer, e.g. a polyethylene layer which optionally contains an anti-halation dye or pigment. It is also possible to use an organic resin support e.g. cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene tereph-

25 thalate) or poly(ethylene naphthalate) film, polycarbonate film, polyvinylchloride film or poly-Alpha-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.07 and 0.35 mm. These organic resin supports are preferably coated with a subbing layer which can contain water insoluble particles such as silica or titanium dioxide.

The photographic material containing tabular grains prepared according to the present invention can be imagewise exposed by any convenient radiation source in accordance with its specific application.

Of course processing conditions and composition of processing solutions are dependent from the specific type of photographic material in which the tabular grains prepared according to the present invention are applied. For example, in a preferred embodiment of materials for X-ray diagnostic purposes said materials may be adapted to rapid processing conditions. Preferably an automatically operating processing apparatus is used provided with a system for auto-

- 35 matic regeneration of the processing solutions. The forehardened material may be processed using one-part package chemistry or three-part package chemistry, depending on the processing application determining the degree of hardening required in said processing cycle. Applications within total processing times of 30 seconds and lower up to 90 seconds, known as common praxis, are possible. From an ecological point of view it is e.g. possible to use sodium thiosulphate instead of ammonium thiosulphate.
- 40 By the method of this invention a silver halide emulsion is thus provided having a covering power as high as possible for different hardening levels of the layer material wherein tabular grains rich in silver bromide are coated in gelatinous emulsion form, accounting for at least 70 % of the total projective area of all grains. Besides tabular grains rich in silver bromide it has been established that also with silver halide grains rich in silver chloride the same advantageous characteristics are obtained, be it to a slightly lesser extent.
- 45 The following examples illustrate the invention without however limiting it thereto.

#### **EXAMPLES**

All tabular grains were precipitated using the double jet technique with control of the pAg value, said value being defined as the negative logarithm of the silver ion concentration.

After precipitation, every example was analysed using shadowed carbon replicas obtained with an electron microscope. For each example a minimum of hundred grains were measured and the following characteristics were then calculated :

- 55 the number of tabular grains were calculated, a tabular grain being defined as a grain with two parallel main planes and a ratio between the diameter and the thickness of the grains of at least 2, with
  - the diameter being the diameter of a circle having an equivalent projective surface area of the grain and
  - the thickness being the distance between the main planes of the flat tabular crystals

A characterization of the crystal population of an emulsion was given by

- average diameter size CD: calculated as the average by number from the diameters of the tabular grains.
- coefficient of variation of the tabular grains: calculated as the ratio between the standard deviation of the average diameter and the average diameter
- average thickness T: calculated as the average by number from the distance between the main planes measured for all crystals
- aspect ratio: as the mean ratio calculated from the calculated diameter and the calculated thickness of all individual tabular grains
- 10 percentage of the total projective surface: part of the total projective area covered by the tabular grains in percentage.

It is known that in the total grain population an increased number of tabular grains rich in bromide is obtained if use is made in the preparation method of oxidised gelatin (see US-A 4,713,320 and RD No. 29945). This is illustrated in Example 1.

15 Example

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# Example 1.

Emulsions Nos. 1-2 are differing in the type of gelatines used, wherein for both emulsions said type is the same in the nucleation step and in the crystal growth step (gelatin GI). Amounts of methionine in Emulsions Nos. 1-2, prepared in the presence of differing types of gelatin, are summarised in Table 1 under MC (methionine content).

For all examples three solutions were used during the precipitation:

Solution 1: 2.450 litre of an aqueous solution containing 500 grams of silver nitrate.

Solution 2: 0.858 litre of an aqueous solution containing 350 grams of potassium bromide.

Solution 3 : 1.592 litre of an aqueous solution containing 341 grams of potassium bromide and 7.5 grams of potassium iodide.

Emulsions Nos. 1-2:

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Preparation steps:

Nucleation step:

- 35 12 ml of solutions 1 and 2 were introduced into a reaction vessel in 9 seconds using the double jet technique. Said reaction vessel initially contained 3000 ml of distilled water at 45°C, 1.5 grams of potassium bromide and 7.5 grams of gelatin-Gl (pH = 1.8; pBr = 2.39). After one minute the reaction temperature of this mixture was raised to 70°C in 25 minutes and a solution of 50 grams of gelatin-Gl in 500 ml of distilled water were added. After 10 minutes the neutralisation step was started after adjustment of pH to a value of 6.0.
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Neutralisation step:

Solution 1 was added to the reaction vessel at a rate of 7.5 ml per minute in order to reach a pAg value of 8.58, whereafter the first growth step was started.

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First growth step:

A double jet precipitation was started using solutions 1 and 2 which continued for 44 minutes 36 seconds. During this precipitation, the pAg value was kept constant at 8.58. The flowing rate of solution 1 was 7.5 ml per minute at the start, linearly increasing to 30.0 ml per minute at the end of the precipitation. Thereafter the second neutralisation step was

50 linearly increasing to 30.0 ml per minute at the end of the precipitation. There started.

Second growth step:

<sup>55</sup> 1592 ml of solution 1 was injected into the reaction vessel at a rate of 7.5 ml per minute at the start, linearly increasing to 40.0 ml per minute at the end of the precipitation. The pAg was kept constant at 8.58 using solution 3 for 63 minutes and 57 seconds.

Table 1 summarises the characteristics of the tabular grains measured from photographs taken with electron micro-

#### scopic techniques. Moreover the procentual amount by number of non-tabular grains is given (% NT).

Table 1

Emulsion No.	MC (GI) (µmole/g)	CD (µm)	Τ (μm)	% NT
1	7.8	1.50	0.11	10
2	45.6	2.40	0.11	35

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It is clear from Table 1 that the use of oxidised gelatin provides a smaller procentual amount by number of non-tabular grains. Further it is clear that there is no variation in average grain thickness as a function of the types of gelatin used (both Emulsions Nos. 1 and 2 have an average thickness of 0.11 μm).

#### 15 Example 2.

For all examples three solutions were used during the precipitation:

Solution 1: 1.5 litre of an aqueous solution containing 500 grams of silver nitrate.

20 Solution 2: 1.5 litre of an aqueous solution containing 350 grams of potassium bromide. Solution 3 : 1.5 litre of an aqueous solution containing 341 grams of potassium bromide and 7.5 grams of potassium iodide.

Emulsions Nos. 3-7:

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Emulsions are differing in the type of gelatin used, being the same in the step of nucleation as in the step of crystal growth (GI-gelatin). Methionine content (MC) for the gelatins used in Emulsions Nos. 3-7 are summarised in Table 2.

Preparation steps:

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Nucleation step:

36 ml of solutions 1 and 2 were introduced into a reaction vessel in 28 seconds using the double jet technique. Said reaction vessel initially contained 2127 ml of distilled water at 51°C, 11.5 grams of potassium bromide and 12.5 grams of gelatin-GI. After one minute the reaction temperature of this mixture was raised to 70°C in 20 minutes and a solution of 47.5 grams of gelatin-GI in 475 ml of distilled water were added. After 10 minutes the neutralisation step was started.

Neutralisation step:

40 Solution 1 was added to the reaction vessel at a rate of 7.5 ml per minute to reach a pAg value of 8.85 (0 mV vs. sat. Ag/AgCl reference electrode), whereafter the first growth step was started.

First growth step:

- 45 A double jet precipitation was started using solutions 1 and 2 which continued for 31 minutes 36 seconds. During this precipitation, the pAg value was kept constant at 8.85 (0 mV). The flowing rate of solution 1 was 7.5 ml per minute at the start, linearly increasing to 22.5 ml per minute at the end of the precipitation. Thereafter the second neutralisation step was started.
- 50 Second neutralisation step:

Solution 1 was added to the reaction vessel at a rate of 7.5 ml per minute in order to reach a pAg value of 7.38, whereafter the precipitation further continued with a second growth step.

55 Second growth step:

975 ml of solution 1 was injected into the reaction vessel at a rate of 7.5 ml per minute at the start, linearly increasing to 37.5 ml per minute at the end of the precipitation. The pAg was kept constant at 7.38 using solution 3 for 41 minutes

and 20 seconds.

The emulsion was flocculated after addition of polystyrene sulphonic acid, acidification to a pH value of 3.0. After sedimentation the mother liquid was removed, distilled water added and remaining salts were washed out after repeating this procedure.

- The emulsion was redispersed and was chemically ripened to an optimal fog-sensitivity relationship after addition 5 of a compounds providing sulphur and gold as chemical sensitisers. Anhydro-5,5'-dichloro-3,3'-bis-(n.sulfobutyl)-9ethyloxacarbo-cyanine hydroxide was added as a green sensitiser. Each emulsion was stabilized with 4-hydroxy-6methyl-1,3,3a,7-tetraazaindene and after addition of the normal coating additives the solutions were coated simultaneously together with a protective layer containing 1.1 g gelatine per m<sup>2</sup> per side on both sides of a polyethylene terephthalate film support having a thickness of 175 µm. The resulting photographic material contained per side an amount of 10
- silver halide corresponding to 3.90 grams of AgNO<sub>3</sub> per m<sup>2</sup>. Hardening of the layers was performed with formaldehyde.

Exposure, sensitometric and densitometric data:

- Samples of these coatings were exposed with green light of 540 nm during 0.1 seconds using a continuous wedge and 15 were processed during the 90 seconds cycle described below. The density as a function of the light dose was measured and therefrom were determined the following parameters:
  - fog level F (with an accuracy of 0.001 density),
- sensitivity S at a density of 1 above fog (in log(Exposure): a decrease with a factor of 0.30 is indicative for an 20 increase of sensitivity with a factor of 2),
  - the contrast C, calculated between the densities 1.0 and 2.5 above fog.

The processing occurred in a glutaraldehyde containing hydroquinone/1-phenyl-3-pyrazolidinone developer marketed by Agfa-Gevaert N.V. under the trade name G138. Fixation was carried out in fixer G334, also marketed by Agfa-25 Gevaert N.V..

Processing conditions and composition of developers.

processing machine : CURIX 402 (Agfa-Gevaert trade name) with the following time (in seconds (sec.)) and tem-30 perature (in °C) characteristics:

3.4 sec.
23.4 sec./ 35°C high or low activity developer
3.8 sec.
15.7 sec./ 35°C in fixer AGFA G334 (trade name)
3.8 sec.
15.7 sec./ 20°C.
32.2 sec. (cross-over time included)
98.0 sec.
2 1 1 3

Table 2 summarises the characteristics of the gelatin used as set forth hereinbefore, the sensitivity and contrast of the samples after processing and the covering power (CP) calculated from the ratio of maximum density and grams of coated silver before processing.

Differences in size of the crystals prepared in differing gelatines for the differing emulsions are summarised in Table 50 1, wherein an average crystal diameter (CD) as well as an average thickness (T) is given for the crystals of each emulsion. An average aspect ratio can be calculated from the ratio between CD and T and is approximately 6.1. An average coefficient of variation of about 0.30 for every emulsion could also be calculated.

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From Table 2 it can be concluded that tabular grain emulsion crystals prepared in gelatin having a lower amount of methionine provide a lower covering power and a lower gradation (indicated as contrast C) if compared with crystals prepared in gelatin having higher amounts of methionine per gram of gelatin (see especially Nos. 6 and 7).

## Example 3.

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20 Emulsions Nos. 8-9 were prepared with types of gelatin differing in methionine content in the nucleation step (GI) vs. in the growth step (GII).

Emulsions Nos. 8-9 were prepared in the same way as Emulsions Nos. 1-2 in Example 1, except for the types of gelatin, differing in methionine content in the nucleation step (GI) versus in the growth step (GII).

Amounts of methionine in the gelatins GI and GII respectively, used in Emulsions Nos. 8-9, are summarised in Table 3. The mean (average) methionine content of the gelatin at the end of the precipitation is given in Table 3 (MC).

The emulsions were flocculated and washed, followed by redispersion, chemical ripening and spectral sensitisation as described for the Emulsions in Example 2 hereinbefore.

Each emulsion was stabilized with 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and after addition of the normal coating additives the solutions were coated simultaneously together with a protective layer containing 1.1 g gelatine per m<sup>2</sup> per

30 side on both sides of a polyethylene terephthalate film support having a thickness of 175 μm. The resulting photographic material contained per side an amount of silver halide corresponding to 3.90 grams of AgNO<sub>3</sub> per m<sup>2</sup>. Hardening of the layers was performed with bis-vinyl-sulphonyl-methylether (BVSME).

Exposure, sensitometric and densitometric data: see Example 2. The processing occurred in the developer containing glutaraldehyde marketed by Agfa-Gevaert N.V. under the trade name G138; fixation was carried out in the fixer, containing aluminum salt, named fixer G334, also marketed by Agfa-Gevaert N.V. just as in Example 2. Processing

conditions were the same as in Example 2.

Table 3 summarises the characteristics of the gelatins used as set forth hereinbefore: as a methionine content the content of the gelatin as a whole (sum of GI + GII) is given; moreover the use of oxidised (OX) or non-oxidised (NOX) gelatin for GI and/or for GII is indicated. Further grain characteristics are listed as measured from photographs taken with electron microscopic techniques, as well as the procentual amount by number of non-tabular grains.

40 with electron microscopic techniques, as well as the procentual amount by number of non-tabular grains. Further the sensitivity S, fog F and contrast C of the samples after processing, the covering power (CP) and differences in size of the crystals prepared in differing gelatines for the different emulsions are given, just as in Example 2.

Em No	GI/GII µmol/g	MC	F	S	С	СР	CD	Т	% NT
8	OX/OX 7.8	7.8	0.077	1.63	5.06	0.70	1.50	0.10	10
9	OX/NOX 40.7	40.7	0.050	1.62	6.16	0.73	1.50	0.10	15

Table 3

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From these data and from Table 1 it can be concluded that tabular grain emulsion crystals prepared in gelatin having a lower amount of methionine (OX) in the nucleation step have a higher amount of (hexagonal) tabular grains. Further addition of said oxidised gelatin (OX) provides a lower covering power and a lower shoulder gradation if compared with crystals prepared in gelatin having higher amounts of methionine per gram of gelatin during the growth step (see Examples 2 and 3). If non-oxidised (NOX) gelatin is used in the nucleation step, non-tabular grains are occurring in an increasing amount (Emulsions Nos. 1 and 2). The thickness of the tabular grains however remains unchanged.

In the present invention the advantages of the use of oxidised gelatin (higher amount of tabular crystals) and the

Em. No.	GI (μmol/g)	F	S	С	C.P.	CD	Т
3	45.6	0.068	1.60	3.31	0.49	1.10	0.19
4	41.3	0.034	1.64	3.33	0.51	1.30	0.19
5	26.2	0.047	1.51	3.08	0.49	1.10	0.19
6	7.8	0.031	1.69	2.92	0.45	1.30	0.18
7	7.2	0.044	1.69	2.69	0.44	1.30	0.20

unexpected advantages of non-oxidised gelatin (higher contrast and higher covering power) are combined by adding oxidised gelatin in the nucleation step and by adding non-oxidised gelatin during the growth step.

### Claims

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- 1. Method for preparing an emulsion having grains rich in silver bromide in the presence of gelatin as a protective colloid, wherein at least 70 % of the total projected area of all grains is provided by tabular grains, said method comprising following steps :
- preparing in a reaction vessel a dispersion medium containing gelatin having less than 30 μmoles of methionine per gram,
  - precipitating therein silver halide crystal nuclei by double-jet precipitation of an aqueous silver nitrate and an
    aqueous solution comprising halide ions, wherein less than 10 % by weight of the total amount of silver nitrate
    used is consumed,
  - adding to said reaction vessel gelatin having 30 or more μmoles of methionine per gram,
    - growing said silver halide crystal nuclei by further precipitation of silver halide by means of double-jet precipitation of an aqueous silver nitrate solution and an aqueous solution comprising halide ions, wherein more than 90 % by weight of the total amount of silver nitrate is consumed, and wherein said tabular grains exhibit
    - an average aspect ratio of at least 2:1;
  - an average thickness of from more than 0.07 μm;
  - a coefficient of variation of the grain size distribution of tabular grains of less than 0.40.
  - 2. Method according to claim 1, wherein said grains rich in silver bromide are composed of silver bromide, silver bromoiodide or silver bromochloroiodide.
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3. Method according to claim 2, wherein in said silver bromoiodide or silver bromochloroiodide iodide is present in an amount of up to 3 mole %.

4. Method according to claim 2 or 3, wherein iodide is provided by means of an iodide releasing agent.

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- 5. Method according to any of claims 1 to 4, wherein a ratio by weight of gelatin having less than 30 μmoles of methionine per gram to gelatin having 30 or more μmoles of methionine per gram is from 1:5 to 1:50.
- 6. Method according to any of claims 1 to 5, wherein the said coefficient of variation of grain size distribution of said tabular grains is between 0.10 and 0.20.
- 7. Method according to any of claims 1 to 6, wherein the average thickness of the said tabular grains is up to 0.20 µm.
- 8. Gelatinous emulsion having silver bromide, silver bromoiodide or silver bromochloroiodide grains, wherein at least
   70 % of total projected area of all grains is provided by tabular grains having an average aspect ratio of at least 2, an average thickness of more than 0.07 µm and wherein gelatin contains methionine in an average amount of from 25 to 42.5 µmoles per gram of said gelatin.
- 9. Photographic material comprising a support and on one or on both sides thereof one or more silver halide emulsion
   45 layer(s) coated from a gelatinous emulsion according to claim 8.
  - **10.** Photographic material according to claim 9, wherein said photographic material is a single-side or double-side coated radiographic material.

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number EP 97 20 2990

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