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(54) **Low silver halide radiographic elements for enhanced wet processing**

(57) A radiographic element comprises a support having disposed on each side thereof, a silver halide emulsion unit that comprises silver halide grains and a gelatino-vehicle. The silver halide grains comprise at least 95 mol% bromide based on total silver, at least 50% of the silver halide grain projected area being provided by tabular grains having an average aspect ratio greater than 8. The grains also have a thickness that is no greater than 0.10 μm and an average grain diameter of from about 1.5 to about 3 μm. The coverage of silver in each silver halide emulsion unit is no more than 11 mg/dm^2, and the coverage of the gelatino-vehicle in each silver halide emulsion unit is no more than 11 mg/dm^2.

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Description

[0001] This invention relates to radiography. More specifically, the invention relates to silver halide elements having relatively lower silver and binder coverage that can be processed quickly with lower strength processing solutions.

Definitions:

[0002] The term "contrast" as herein employed indicates the average contrast (also referred to as γ) derived from a characteristic curve of a radiographic element using as a first reference point (1) a density (D_1) of 0.25 above minimum density and as a second reference point (2) a density (D_2) of 2.0 above minimum density, where contrast is ΔD (i.e. 1.75) $\div$ $\Delta \log_{10} E$ ($\log_{10} E_2 - \log_{10} E_1$), E_1 and E_2 being the exposure levels at the reference points (1) and (2).

[0003] The term "dual-coated" is employed to indicate radiographic elements having image forming layer units disposed on opposite sides of a support.

[0004] The terms "front" and "back" refer to features or elements nearer to and farther from, respectively, the X-radiation source than the support of the radiographic element.

[0005] The term "fully forehardened" is employed to indicate the forehardening of hydrophilic colloid layers to a level that limits the weight gain of a radiographic element to less than 120 percent of its original (dry) weight in the course of wet processing. The weight gain is almost entirely attributable to the ingestion of water during such processing.

[0006] The term "rapid access processing" is employed to indicate dry-to-dry processing of a radiographic element in 45 seconds or less. That is, 45 seconds or less elapse from the time a dry imagewise exposed radiographic element enters a wet processor until it emerges as a dry fully processed element.

[0007] In all references to silver halide grains and emulsions containing two or more halides, the halides are named in order of ascending concentrations.

[0008] The "aspect ratio" of a silver halide grain is the ratio of its equivalent circular diameter (ECD) to its thickness. The ECD of a grain is the diameter of a circle having an area equal to the projected area of the grain.

[0009] The "coefficient of variation" (COV) of silver halide grain size (ECD) is defined as 100 times the standard deviation of grain ECD divided by mean grain ECD.

[0010] The term "tabular grain" refers to a silver halide grain having two parallel crystal faces that are clearly larger than any remaining crystal faces and an aspect ratio of at least 2.

[0011] The term "tabular grain emulsion" refers to an emulsion in which tabular grains account for greater than 50% of total grain projected area.

[0012] The term "covering power" is used to indicate 100 times the ratio of maximum density to developed silver measured in mg/dm^2.

[0013] The term "colder" in referring to image tone is used to mean an image tone that has a more negative CIELAB b* value measured at a density of 1.0 above minimum density, where an optimally "cold" image tone is -6.5 or more negative. The measurement technique is described by Billmeyer and Saltzman, Principles of Color Technology, 2nd Ed., Wiley, New York, 1981, at Chapter 3. The b* values describe the yellowness vs. blueness of an image with more positive values indicating a tendency toward greater yellowness (image warmth).

[0014] The term "rare earth" is used to indicate elements having an atomic number of 39 or 57 through 71.

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Background:

[0016] In medical diagnostic radiography, the object is to obtain a viewable silver image from which a medical diagnosis can be made while exposing the patient to a minimal dose of X-radiation. Patient exposure to X-radiation is minimized by employing a dual-coated radiographic element in combination with front and back fluorescent intensifying screens. A portion of the X-radiation transmitted through the patient's anatomy is absorbed by each of the front and back intensifying screens. Each screen emits light in response to X-radiation exposure, and the emitted light from the front and back screens imagewise exposes the front and back emulsion layers of the dual-coated radiographic element. With this arrangement, patient exposure to X-radiation can be reduced to about 5 percent of the X-radiation exposure level that would be required for comparable imaging using a single emulsion layer and no intensifying screen.

[0017] Unlike photographic images, which are taken in small formats and then enlarged for viewing, radiographic images are normally viewed without enlargement. Thus, very large formats by photographic standards are required. Further, unlike color photography, wherein silver is reclaimed in processing, the silver in radiographic elements is often not reclaimed for years, since the images are required to be available to substantiate diagnoses. Further, usually a number of images are obtained when subject matter of pathological interest is observed.

[0018] Thus, there has been in medical diagnostic imaging a long-standing need to minimize to the extent feasible the silver contained in the elements. Silver coating coverage reductions have been limited by performance requirements. Sufficient silver is required to achieve a maximum image density (D_{max}) of at least 3.0 and to maintain an average contrast (γ) of at least 2.7.

[0019] An early approach to reducing silver coating coverage while satisfying these performance requirements was to employ organic covering power increasing addenda in the emulsions. The water soluble dextran, poly(vinylpyrrolidone) and polyacrylamide have been incorporated into emulsion layers to increase covering power, as illustrated by US-A-3,271,158 (Allentoff et al), US-A-3,272,631 (Garrett et al) and US-A-3,514,289 (Goffe et al). Other covering power enhancing compounds are disclosed by *Research Disclosure*, Vol. 184, August 1979, Item 18431, E. Stabilization of Radiographic Materials Comprising Covering Power Addenda.

[0020] Another common approach was to maximize covering power by employing an organic covering power enhancer and to foreharden the emulsion layers only partially, relying on a prehardener to complete hardening in the course of processing.

[0021] US-A-4,414,304 (Dickerson et al) teaches that tabular grain emulsions provide sufficient covering power to be fully forehardened. At levels of hardening high enough to allow processing solution hardener to be eliminated, the covering power of the tabular grain emulsions of Dickerson et al is shown to vary little as a function of hardening. Further, Dickerson et al demonstrated that covering power increases as the average thickness of the tabular grains decreases.

[0022] When attempts were made to minimize silver coating coverage employing tabular grain emulsions, reducing the thickness of the tabular rains led to warmer image tones which is considered a problem. This has limited the minimum tabular grain thickness that can be employed in radiographic elements. This has in turn resulted in silver coating coverage that, while lower than those employed prior to the use of tabular grain emulsions, are still higher than the minimum values that are capable of otherwise satisfying image structure requirements.

[0023] Another problem that has arisen from the use of tabular grain emulsions is residual dye stain. Higher ratios of spectral sensitizing dye to silver are required to optimally sensitize tabular grain emulsions as compared to nontabular grain emulsions. This results in higher concentrations of spectral sensitizing dye that must be removed during processing to avoid residual dye stain.

[0024] Some of these problems were overcome using the teaching of US-A-5,800,976 (Dickerson et al) wherein lowered silver coverage on each side of the support (for example, 11.8 mg/dm^2) is possible by using a combination of support and emulsion characteristics. Specifically, this patent teaches that lower silver coverage is possible by using a neutral density support, at least 90% tabular grains, a covering power enhancing compound (dextran or a polyacrylamide) in admixture with the gelatino-vehicle, and partial hardening of the gelatino-vehicle.

[0025] While the radiographic films described in this patent represent an important advance in the art, there is a further need to reduce silver and gelatino-vehicle coverage in order to provide more rapid wet processing in a variety of processing systems. Heretofore, it was believed that lower film coverage and faster processing would lead to lower D_{max} and contrast and unacceptable drying times. The present invention overcomes these problems and provides an opportunity for novel photoprocessing systems, that is compatible photoprocessing chemistry and equipment.

[0026] To overcome the noted problems, the present invention provides a radiographic element comprising a support having disposed on each side thereof, a silver halide emulsion unit that comprises silver halide grains and a gelatino-vehicle, the silver halide grains comprising at least 95 mol% bromide based on total silver, at least 50% of the silver halide grain projected area being provided by tabular grains having an average aspect ratio greater than 8, a thickness no greater than 0.10 μm, and an average grain diameter of from about 1.5 to about 3 μm,

the element characterized wherein the coverage of silver in each silver halide emulsion unit is no more than 11 mg/dm^2, and the coverage of the gelatino-vehicle in each silver halide emulsion unit is no more than 11 mg/dm^2.

[0027] The present invention provides a low silver radiographic element that is effectively processed in a variety of wet processing systems to provide an image with low fog and dye stain. Despite the lower silver in the elements, we unexpectedly discovered that the elements provided acceptable sensitometric results (that is, speed, contrast and D_{max}) even when processed using weaker or more dilute processing compositions. By "weaker" is meant that the processing compositions contain lower concentrations of the photographic reagents (for example, developing and fixing agents) needed for image formation. In addition, we discovered that the processed elements could be rapidly dried despite the use of lowered amounts of hardener for layers containing the gelatino-vehicle.

[0028] Thus, the combination of features of the elements of this invention enable a user to obtain suitable black-and-white images with either weaker processing solutions, or to use shorter processing times with conventional processing compositions. Thus, the elements provide greater flexibility in their use.

[0029] The radiographic elements of this invention comprise a support having a single silver halide emulsion unit on each side thereof. Such units include one or more silver halide emulsion layers. Further details of the support and silver halide emulsion units are provided below. In operation, such an element is generally included in an exposure assembly that also includes one or more intensifying screens in front or back of the element. The element and front and back screens are usually mounted in direct contact in a suitable cassette. X-radiation in an imagewise pattern is passed through and partially absorbed in the front intensifying screen, and a portion of the absorbed X-radiation is re-emitted as a visible light image tat exposes the silver halide emulsion units of the element. X-radiation that is not absorbed by the front screen passes through the element with minimal absorption to reach the back intensifying screen. A substantial portion of that radiation is absorbed by the back screen and a portion of it is re-emitted as visible light image that also exposes the silver halide emulsion units of the element.

[0030] In their simplest construction, the radiographic elements of this invention include a single silver halide emulsion layer on each side of the support. Preferably, however, there is also an interlayer and a protective overcoat on each side the support. General features of radiographic films are described in US-A-5,871,892 (Dickerson et al), with respect to those films.

[0031] Any conventional transparent radiographic or photographic film support can be employed in constructing the elements of this invention. Radiographic film supports usually exhibit these specific features: (1) they are constructed of polyesters to maximize dimensional integrity and (2) they are blue tinted to contribute the cold (blue-black) image tone sought in the fully processed films. Radiographic film supports, including the incorporated blue dyes that contribute to cold image tones, are described in *Research Disclosure*, Item 18431, cited above, Section XII. Film Supports. *Research Disclosure*, Vol. 365, September 1994, Item 36544, Section XV. Supports, illustrates in paragraph (2) suitable subbing layers to facilitate adhesion of hydrophilic colloids to the support. Although the types of transparent films set out in Section XV, paragraphs (4), (7) and (9) are contemplated, due to their superior dimensional stability, the transparent films preferred are polyester films, illustrated in Section XV, paragraph (8). Poly(ethylene terephthalate) and poly(ethylene naphthalate) are specifically preferred polyester film supports.

[0032] The transparent support can be subbed using conventional subbing materials that would be readily apparent to one skilled in the art.

[0033] The emulsion layers contain the light-sensitive high silver bromide relied upon for image formation. To facilitate rapid access processing the grains preferably contain less than 2 mol% (mole percent) iodide, based on total silver. The silver halide grains are predominantly silver bromide in content. Thus, the grains can be composed of silver bromide, silver iodobromide, silver chlorobromide, silver iodochlorobromide, silver chloroiodobromide or silver iodochlorobromide as long as bromide is present in an amount of at least 95 mol% (preferably at least 98 mol%) based on total silver content.

[0034] In addition to the advantages obtained by composition selection described above it is specifically contemplated to employ silver halide grains that exhibit a coefficient of variation (COV) of grain ECD of less than 20% and, preferably, less than 10%. It is preferred to employ a grain population that is as highly monodisperse as can be conveniently realized.

[0035] In addition, at least 50% (and preferably at least 70%) of the silver halide grain projected area is provided by tabular grains having an average aspect ratio greater than 8, and preferably greater than 12. The average thickness of the grains is generally at least 0.06 and no more than 0.10 μm, and preferably at least 0.07 and no more than 0.09 μm. The average grain diameter is from about 1.5 to about 3 μm, and preferably from about 1.8 to about 2.4 μm.

[0036] Tabular grain emulsions that satisfy high bromide grain requirements and gelatino-vehicle requirements, except that the gelatino-vehicle is fully forehardened, are described in greater detail in the following patents:

Dickerson	US-A-4,414,310,
Abbott et al	US-A-4,425,425,
Abbott et al	US-A-4,425,426,
Kofron et al	US-A-4,439,520,
Wilgus et al	US-A-4,434,226,
Maskasky	US-A-4,435,501,
Maskasky	US-A-4,713,320,
Dickerson et al	US-A-4,803,150,
Dickerson et al	US-A-4,900,355,
Dickerson et al	US-A-4,994,355,
Dickerson et al	US-A-4,997,750,
Bunch et al	US-A-5,021,327,
Tsaur et al	US-A-5,147,771,
Tsaur et al	US-A-5,147,772,
Tsaur et al	US-A-5,147,773,
Tsaur et al	US-A-5,171,659,
Dickerson et al	US-A-5,252,442,
Dickerson	US-A-5,391,469,
Dickerson et al	US-A-5,399,470,
Maskasky	US-A-5,411,853,

Maskasky	US-A-5,418,125,
Daubendiek et al	US-A-5,494,789,
Olm et al	US-A-5,503,970,
Wen et al	US-A-5,536,632,
King et al	US-A-5,518,872,
Fenton et al	US-A-5,567,580,
Daubendiek et al	US-A-5,573,902,
Dickerson	US-A-5,576,156,
Daubendiek et al	US-A-5,576,168,
Olm et al	US-A-5,576,171, and
Deaton et al	US-A-5,582,965.

The patents to Abbott et al, Fenton et al, Dickerson and Dickerson et al are cited to show conventional element features in addition to the gelatino-vehicle, high bromide tabular grain emulsions and other critical features of the present invention.

[0037] Film contrast can be raised by the incorporation of one or more contrast enhancing dopants. Rhodium, cadmium, lead and bismuth are all well known to increase contrast by restraining toe development. The toxicity of cadmium has precluded its continued use. Rhodium is most commonly employed to increase contrast and is specifically preferred. Contrast enhancing concentrations are known to range from as low 10^{-9} mole/Ag mole. Rhodium concentrations up to 5 X 10^{-3} mole/Ag mole are specifically contemplated. A specifically preferred rhodium doping level is from 1 X 10^{-6} to 1 X 10^{-4} mole/Ag mole.

[0038] A variety of other dopants are known, individually and in combination, to improve contrast as well as other common properties, such as speed and reciprocity characteristics. Dopants capable providing "shallow electron trapping" sites, commonly referred to as SET dopants, are specifically contemplated. SET dopants are described in *Research Disclosure*, Vol. 367, Nov. 1994, Item 36736. Iridium dopants are very commonly employed to decrease reciprocity failure. A summary of conventional dopants to improve speed, reciprocity and other imaging characteristics is provided by *Research Disclosure*, Item 36544, cited above, Section I. Emulsion grains and their preparation, sub-section D. Grain modifying conditions and adjustments, paragraphs (3), (4) and (5).

[0039] Low COV emulsions can be selected from among those prepared by conventional batch double-jet precipitation techniques. A general summary of silver halide emulsions and their preparation is provided by *Research Disclosure*, Item 36544, cited above, Section I. Emulsion grains and their preparation. After precipitation and before chemical sensitization the emulsions can be washed by any convenient conventional technique using techniques disclosed by *Research Disclosure*, Item 36544, cited above, Section III. Emulsion washing.

[0040] The emulsions can be chemically sensitized by any convenient conventional technique as illustrated by *Research Disclosure*, Item 36544, Section IV. Chemical sensitization. Sulfur and gold sensitizations are specifically contemplated.

[0041] Both silver bromide and silver iodide have significant native sensitivity within the blue portion of the visible spectrum. Hence, when the emulsion grains contain high (>50 mol%, based on total silver) bromide concentrations, spectral sensitization of the grains is not essential, tough still preferred. It is specifically contemplated that one or more spectral sensitizing dyes will be absorbed to the surfaces of the grains to impart or increase their light-sensitivity. Ideally the maximum absorption of the spectral sensitizing dye is matched (e.g., within ± 10 nm) to the principal emission band or bands of the fluorescent intensifying screen. In practice any spectral sensitizing dye can be employed which, as coated, exhibits a half peak absorption bandwidth that overlaps the principal spectral region(s) of emission by a fluorescent intensifying screen intended to be used with the first radiographic film.

[0042] A wide variety of conventional spectral sensitizing dyes are known having absorption maxima extending throughout the near ultraviolet (300 to 400 nm), visible (400 to 700 nm) and near infrared (700 to 1000 nm) regions of the spectrum. Specific illustrations of conventional spectral sensitizing dyes is provided by *Research Disclosure*, Item 18431, Section X. Spectral Sensitization, and Item 36544, Section V. Spectral sensitization and desensitization, A. Sensitizing dyes.

[0043] Instability which increases minimum density in negative-type emulsion coatings (i.e., fog) can be protected against by incorporation of stabilizers, antifoggants, antikinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Such addenda are illustrated by *Research Disclosure*, Item 36544, Section VII. Antifoggants and stabilizers, and Item 18431, Section II. Emulsion Stabilizers, Antifoggants and Antikinking Agents.

[0044] It is also preferred that the silver halide emulsions include one or more covering power enhancing compounds adsorbed to surfaces of the silver halide grains. A number of such materials are known in the art, but preferred covering power enhancing compounds contain at least one divalent sulfur atom that can take the form of a -S- or =S moiety. Such compounds include, but are not limited to, 5-mercapotetrazoles, dithioxotriazoles, mercapto-substituted tetraazaindenes, and others described in US-A-5,800,976 (noted above) for the teaching of the sulfur-containing covering power enhancing compounds. Such compounds are generally present at concentrations of at least 20 mg/silver mole, and preferably of at least 30 mg/silver mole. The concentration can generally be as much as 2000 mg/silver mole and preferably as much as 700 mg/silver mole.

[0045] It is also preferred that the silver halide emulsion on each side of the support includes dextran or polyacrylamide as water-soluble polymers that can also enhance covering power. These polymers are generally present in an amount of at least 0.1:1 weight ratio to the gelatino-vehicle (described below), and preferably in an amount of from about 0.3:1 to about 0.5:1 weight ratio to the gelatino-vehicle. The dextran or polyacrylamide can be present in an amount of up to 5 mg/dm^2, and preferably at from about 2 to about a 4 mg/dm^2. The amount of covering power enhancing compounds on the two sides of the support can be the same or different.

[0046] The silver halide emulsion and other layers forming the imaging units on opposite sides of the support of the radiographic element contain conventional hydrophilic colloid vehicles (peptizers and binders) that are typically gelatin or a gelatin derivative (identified herein as "gelatino-vehicles"). Conventional gelatino-vehicles and related layer features are disclosed in *Research Disclosure*, Item 36544, Section II. Vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda. The emulsions themselves can contain peptizers of the type set out in Section II. noted above, paragraph A. Gelatin and hydrophilic colloid peptizers. The hydrophilic colloid peptizers are also useful as binders and hence are commonly present in much higher concentrations than required to perform the peptizing function alone. The gelatino-vehicle extends also to materials that are not themselves useful as peptizers. The preferred gelatino-vehicles include alkali-treated gelatin, acid-treated gelatin or gelatin derivatives (such as acetylated gelatin and phthalated gelatin).

[0047] To allow maximum density requirements to be satisfied with minimal silver coating coverage it is necessary to limit the forehardening of the gelatino-vehicle. Whereas it has become the typical practice to fully foreharden radiographic elements containing tabular grain emulsions, the radiographic elements of this invention are only partially forehardened. Thus, the amount of hardener in each silver halide emulsion unit is generally at least 0.1% and less than 0.8%, and preferably at least 0.3% and less than 0.6%, based on the total dry weight of the gelatino-vehicle.

[0048] Conventional hardeners can be used for this purpose, including formaldehyde and free dialdehydes such as succinaldehyde and glutaraldehyde, blocked dialdehydes, α-diketones, active esters, sulfonate esters, active halogen compounds, *s*-triazines and diazines, epoxides, aziridines, active olefins having two or more active bonds, blocked active olefins, carbodiimides, isoxazolium salts unsubstituted in the 3-position, esters of 2-alkoxy-N-carboxydihydroquinoline, N-carbamoyl pyridinium salts, carbamoyl oxypyridinium salts, bis(imoniomethyl) ether salts, particularly bis(amidino) ether salts, surface-applied carboxyl-activating hardeners in combination with complex-forming salts, carbamoylonium, carbamoyl pyridinium and carbamoyl oxypyridinium salts in combination with certain aldehyde scavengers, dication ethers, hydroxylamine esters of imidic acid salts and chloroformamidinium salts, hardeners of mixed function such as halogen-substituted aldehyde acids (e.g., mucochloric and mucobromic acids), onium-substituted acroleins, vinyl sulfones containing other hardening functional groups, polymeric hardeners such as dialdehyde starches, and copoly(acrolein-methacrylic acid).

[0049] In each silver halide emulsion unit in the radiographic element, the level of silver is generally at least 8 and no more than 11 mg/dm^2, and preferably at least 9 and no more than 10 mg/dm^2. In addition, the coverage of gelatino-vehicle is generally at least 6 and no more than 11 mg/dm^2, and preferably at least 7.5 and no more than 9.5 mg/dm^2. The amounts of silver and gelatino-vehicle on the two sides of the support can be the same or different.

[0050] The radiographic elements generally include a surface overcoat on each side of the support that are typically provided for physical protection of the emulsion layers. In addition to vehicle features discussed above the overcoats can contain various addenda to modify the physical properties of the overcoats. Such addenda are illustrated by *Research Disclosure*, Item 36544, Section IX. Coating physical property modifying addenda, A. Coating aids, B. Plasticizers and lubricants, C. Antistats, and D. Matting agents. Interlayers that are typically thin hydrophilic colloid layers can be used to provide a separation between the emulsion layers and the surface overcoats. It is quite common to locate some emulsion compatible types of surface overcoat addenda, such as anti-matte particles, in the interlayers.

Example:

Radiographic Element A (Control):

[0051] Radiographic Element A was a DUPLITIZED radiographic element having identical silver halide emulsions on both sides of a blue-tinted 178 μm transparent poly(ethylene terephthalate) film support. Each silver halide emulsion was a green-sensitized high aspect ratio tabular silver bromide emulsion. The term "high aspect ratio" is employed as defined by US-A-4,425,425 (Abbott et al) to require that at least 50% of the total grain projected area be accounted for by tabular grains having a thickness of less than 0.3 μm and having an average aspect ratio greater than 8:1. The emulsion contained silver halide grains having an average grain diameter of 1.8 μm and an average grain thickness of 0.13

μm. It was chemically sensitized with sodium thiosulfate, potassium tetrachloroaurate, sodium thiocyanate and potassium selenocyanate and spectrally sensitized with 400 mg/Ag mol of anhydro-5,5-dichloro-9-ethyl-3,3'-bis(3-sulfopropyl)oxacarbocyanine hydroxide, followed by 300 mg/Ag mol of potassium iodide.

[0052] Over each silver halide emulsion layer was an interlayer and an overcoat. The following formulations show the content of each layer on each side of the support.

Overcoat Formulation	Coverage (mg/dm^2)
Gelatin vehicle	3.4
Methyl methacrylate matte beads	0.14
Carboxymethyl casein	0.57
Colloidal silica	0.57
Polyacrylamide	0.57
Chrome alum	0.025
Resorcinol	0.058
Whale oil lubricant	0.15

Interlayer Formulation	Coverage (mg/dm^2)
Gelatin vehicle	3.4
AgI Lippmann emulsion (0.08 μm)	0.11
Carboxymethyl casein	0.57
Colloidal silica	0.57
Polyacrylamide	0.57
Chrome alum	0.025
Resorcinol	0.058
Nitron	0.044

Emulsion Layer Formulation	Coverage (mg/dm^2)
T-grain emulsion (AgBr 1.8 x 0.13 μm)	18.3
Gelatin vehicle	21.5
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
Potassium nitrate	1.8
Ammonium hexachloropalladate	0.0022
Maleic acid hydrazide	0.0087
Sorbitol	0.53

(continued)

Emulsion Layer Formulation	Coverage (mg/dm^2)
Glycerin	0.57
Potassium bromide	0.14
Resorcinol	0.44
Bisvinylsulfonylmethylether	2.4% based on total gelatin in all layers

Radiographic Element B (Control):

[0053] Radiographic Element B is the same as Element E (Col. 14) described in US-A-5,800,976 (noted above). Thus, it is similar to Radiographic Element A except that a tabular grain emulsion with lower grain thickness was employed and was coated with a total silver coverage of 11.8 mg/dm^2 on each side of the support. The hardener level on each side of the support was 0.8% (based on total gelatin weight).

Radiographic Element C (Invention):

[0054] Radiographic element C is similar to Radiographic Element B except that a tabular grain emulsion with lower grain thickness was employed and was coated with a total silver coverage of 10.6 mg/dm^2 on each side of the support. On each side of the support, the total emulsion layer gelatin coverage was 7.5 mg/dm^2, the dextran coverage was 2.5 mg/dm^2 and the hardener level was 0.4% (based on total gelatin weight). The emulsion employed was a green sensitized high aspect ratio tabular silver bromide emulsion wherein the term "high aspect ratio" is as defined above. The emulsion had an average grain diameter of 2.0 µm and an average grain thickness of 0.07 um. The emulsion was spectrally sensitized with 590 mg/Ag mol of anhydro-5,5-dichloro-9-ethyl-3,3'-bis(3-sulfopropyl)oxacarbocyanine hydroxide, followed by 300 mg/Ag mol of potassium iodide.

[0055] The emulsion layer on each side of the support is more specifically defined as follows. The interlayers and overcoats were identical to those described above for Radiographic Element A.

Emulsion Formulation	Coverage (mg/dm^2)
T-grain emulsion (AgBr 2.0 x 0.07 µm)	10.6
Gelatin	7.5
4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene	2.1 g/Ag mole
4-hydroxy-6-methyl-2-methylmercapto-1,3,3a,7-tetraazaindene	400 mg/Ag mole
2-mercapto-1,3-benzothiazole	30 mg/Ag mole
Potassium nitrate	1.8
Ammonium hexachloropalladate	0.0022
Maleic acid hydrazide	0.0087
Sorbitol	0.53
Glycerin	0.57
Potassium bromide	0.14
Resorcinol	0.44
Dextran P	2.5
Polyacrylamide	2.69
Carboxymethyl casein	1.61
Bisvinylsulfonylmethlyether	0.4 % based on total gelatin in all layers

[0056] Samples of Radiographic Elements A, B and C were exposed on the emulsion side only through a graduated density step tablet using a MacBeth sensitometer for 1/50 second and a 500 watt General Electric DMX projector lamp calibrated to 2650°K filtered with a Coming C4010 filter to simulate a green-emitting X-ray screen exposure.

[0057] Residual dye stain was measured using conventional spectrophotometric methods and calculated as the difference between the density at 505 nm (that corresponds to the dye absorption peak) and the density at 440 nm (that is the density associated with developed silver). This measurement corrects for differences in film fog. The measurements were done on film samples that had been processed without exposure and were nominally clear of developed silver except for fog silver.

[0058] Processing of the exposed film samples for sensitometric evaluation was carried out using a processor commercially available under the trademark KODAK RP X-OMAT film Processor M6A-N. Development was carried out using the following black-and-white developer composition:

Hydroquinone	30 g
Phenidone	1.5 g
KOH	21 g
$NaHCO_3$	7.5 g
$K2SO_3$	44.2 g
$Na_2S_2O_5$	12.6 g
NaBr	35 g
5-Methylbenzotriazole	0.06 g
Glutaraldehyde	4.9 g
Water to 1 liter, pH 10	

[0059] The film samples were in contact with the developer in each instance for less than 90 seconds. Fixing was carried out using KODAK RP X-OMAT LO Fixer and Replenisher fixing composition.

[0060] Rapid processing has evolved over the last several years as a way to increase productivity in busy hospitals without compromising image quality or sensitometric response. Where 90 second processing times were once the standard, below 40 seconds processing is becoming the standard in medical radiography. One such example of a rapid processing system is the commercially available KODAK Rapid Access (RA) processing system that includes a line of X-ray sensitive films available as T-MAT-RA radiographic films that feature fully forehardened emulsions in order to maximize film diffusion rates and minimize film drying. Processing chemistry for this process is also available. As a result of the film being fully forehardened, glutaraldehyde (a common hardening agent) can be removed from the developer solution, resulting in ecological and safety advantages. The developer and fixer designed for this system are Kodak X-OMAT RA/30 chemicals. A commercially available processor that allows for the rapid access capability is the Kodak X-OMAT RA 480 processor. This processor is capable of running in 4 different processing cycles. "Extended" cycle is for 160 seconds, and is used for mammography where longer than normal processing results in higher speed and contrast. "Standard" cycle is 82 seconds, "Rapid Cycle" is 55 seconds and "KWIK/RA" cycle is 40 seconds. A proposed new "Super KWIK" cycle is intended to be 30 seconds. The two KWIK cycles (30 & 40 seconds) use the new RA/30 chemistries while the longer time cycles use standard RP X-OMAT chemistry. The following Table I shows typical processing times (seconds) for these various processing cycles.

TABLE I

Cycle	Extended	Standard	Rapid	KWIK	Super KWIK
Developer	44.9	27.6	15.1	11.1	8.3
Fixer	37.5	18.3	12.9	9.4	7.0
Wash	30.1	15.5	10.4	7.6	5.6
Drying	47.5	21.0	16.6	12.2	9.1
Total	160.0	82.4	55	40.3	30.0

[0061] For the following sensitometric data, optical densities are expressed in terms of diffuse density as measured by an X-rite Model 310TM densitometer that was calibrated to ANSI standard PH 2.19 and was traceable to a National Bureau of Standards calibration step tablet. The characteristic curve (Density vs. log E) was plotted for each radiographic element processed. Speed was measured at a density of 1.0 + Dmin. Contrast was measured as the slope of the curve between a density of Dmin + 0.25 to a density of Dmin + 2.0.

[0062] The "% Drying" was determined by feeding an exposed film flashed to result in a density of 1.0 into an X-ray processor. As the film just exited the drier section, the processor was stopped and the film was removed from the processor. Roller marks from the processor can be seen on the film where the film has not yet dried. Marks from 100% of the rollers in the drier indicate the film has just barely dried. Values less than 100% indicate the film has dried partway into the drier. The lower the value the better the film is for drying.

[0063] The data in the following Table II show that Element C (Invention) exhibited essentially the same sensitometry as Control Element B even though it had extremely low silver coverage compared to Control Element A. Even though Element C, unlike Element B, contained very low hardener levels, it could be processed and dried using the very short KWIK cycle processing times. This is due to the very low gelatin and silver levels used in the element. This shows the versatility of the elements of this invention for use in various processing systems.

TABLE II

Film	Speed	Contrast	Dmax	Dmin	% Drying	Dye Stain
Control A	442	2.6	3.2	.20	65	0.07
Control B	454	2.7	3.2	.20	>100	0.02
Invention C	447	2.6	3.2	.19	65	0.01
% Drying was measured using the KWIK processing cycle.						

Claims

1. A radiographic element comprising a support having disposed on each side thereof, a silver halide emulsion unit that comprises silver halide grains and a gelatino-vehicle, the silver halide grains comprising at least 95 mol% bromide based on total silver, at least 50% of the silver halide grain projected area being provided by tabular grains having an average aspect ratio greater than 8, a thickness no greater than 0.10 μm, and an average grain diameter of from about 1.5 to about 3 μm,

   the element characterized wherein the coverage of silver in each silver halide emulsion unit is no more than 11 mg/dm^2, and the coverage of the gelatino-vehicle in each silver halide emulsion is no more than 11 mg/dm^2.

2. The radiographic element of claim 1 wherein each silver halide emulsion unit comprises from about 0.1 to about 0.8% hardener based on the total dry weight of the gelatino-vehicle.

3. The radiographic element of claim 1 or 2 wherein the coverage of silver in each silver halide emulsion unit is from

about 8 to about 11 mg/dm^2, and the coverage of the gelatino-vehicle in each silver halide emulsion unit is from about 6 to about 11 mg/dm^2.

4. The radiographic element of claim 3 wherein the coverage of silver in each silver halide emulsion unit is from about 9 to about 10 mg/dm^2, and the coverage of the gelatino-vehicle in each silver halide emulsion unit is from about 7.5 to about 9.5 mg/dm^2.

5. The radiographic element of any of claims 1 to 4 wherein at least 70% of the silver halide grain projected area being provided by tabular grains having an average aspect ratio greater than 12, a thickness of from about 0.06 to about 0.10 µm, and an average grain diameter of from about 1.5 to about 3 µm.

6. The radiographic element of any of claims 1 to 5 wherein the silver halide grains comprise at least 98 mol% bromide based on total silver, and less than 2 mol% iodide based on total silver.

7. The radiographic element of any of claims 1 to 6 wherein each of the silver halide emulsion units comprises at least one covering power enhancing compound containing at least one divalent sulfur atom adsorbed to surfaces of the silver halide grains.

8. The radiographic element of any of claims 1 to 7 wherein each of the silver halide emulsion units comprises polyacrylamide or dextran in a weight ratio to the gelatino-vehicle of at least 0.1:1.

9. The radiographic element of claim 8 wherein each of the silver halide emulsion units comprises polyacrylamide or dextran in a weight ratio to the gelatino-vehicle of from about 0.3:1 to about 0.5:1.

10. The radiographic element of any of claims 1 to 7 wherein each of the silver halide emulsion units comprises dextran at a coverage of up to 5 mg/dm^2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 20 1644

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X Y	US 5 876 909 A (HERSHEY ET AL.) 2 March 1999 (1999-03-02) * column 1, line 19 - line 21 * * column 1, line 52 - line 54 * * column 9, line 5 - line 39 * * column 11, line 46 - line 50 * * column 12, line 36 - line 41 * * column 13, line 52 - column 14, line 53 *	1-6,8,9 7,10	G03C1/005 G03C5/16
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 June 2000	Magrizos, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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