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(54) **Silver halide light-sensitive photographic screen-film system with enhanced image quality for rapid processing applications in mammography**

Lichtempfindliches photographisches Schirm/Silberhalogenidfilmsystem mit verbesserter Bildqualität für Schnellverarbeitungsanwendungen in der Mammographie

Système écran/film photographique à l'halogénure d'argent sensible à la lumière avec qualité d'image améliorée pour des applications de traitement rapide en mammographie

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Description

1. Field of the invention.

[0001] This invention relates to a novel screen-film system of a radiographic intensifying screen and a silver halide photographic light-sensitive material, comprising at least one silver halide emulsion layer on only one side of the support.

2. Background of the invention.

[0002] In medical radiography the direct exposure technique is used in mammographic applications, wherein the radiation pattern leaving the patient's breast is registered directly on a film with the use of an intensifying screen.

[0003] No other area of medical X-ray applications demands such a level of contrast and spatial resolution as produced in quality mammography. This explains why single-side coated films are used in this application.

[0004] The success of mammography, whether for screening or diagnosis, depends on the production of high-quality, low-dose images. Image quality determines the accuracy with which various structures are recorded and abnormalities detected. For mammography, films high in contrast are preferred. Most of the mammographic films have a high overall-contrast but also the toe contrast, i.e. the contrast in the region of the lightest areas on the film is important. Dense structures in the breast give rise to pale areas on the mammograms. The shoulder of the sensitometric curve represents the darkest areas on the film or the low density breast tissue. The shoulder contrast is important in mammography, not only because it influences the overall contrast of the curve, but also because some information is available in that part of the image. The skin line becomes visualised, depending on shoulder contrast and maximum density. This is why maximum density should not be lower than 3.60.

[0005] As is generally known for one skilled in the art of photography the sensitometric values and the image quality of a photographic light-sensitive material do not only depend on the characteristics of the emulsion or the composition of the material but are determined also to a considerable extent by the processing conditions. Contrast, speed, and thus also the perceptible detail is affected by processing conditions such as the type of the selected developer, the developer temperature, the degree of development and the condition of the processor. E.g. it is common knowledge that the slope of the characteristic curve of a photographic material increases with increasing degree of development. However once a particular limit has been reached, especially the slope at lower densities decreases with higher degrees of development as the fog caused by development rises.

[0006] On the other hand there is a general trend to enhance the speed of processing, especially in the field of radiography, and therefore interest has been focused on rapid access of radiographs, being vital in diagnosis, with development characteristics as independent as possible from development conditions.

[0007] There is a tendency of further decreasing the total processing time of X-ray materials in particular to less than 60 seconds, e.g., 45 seconds processing and even 38 seconds processing. The requirement is that the sensitometry and image quality with such short processing times should match the sensitometry and image quality of the silver halide photographic light-sensitive material now processed in 90 seconds or in the extended processing cycles used in mammographic applications.

[0008] Hitherto for mammographic applications there is no film available that can be processed within a total processing cycle of 45 or 38 seconds as is possible for other radiographic applications. Processing in such a short length of time inevitably causes archiving problems due to insufficient fixation and sticking phenomena due to drying problems. The archiving problems occur because of the high silver content in silver halide light-sensitive mammographic materials, and it occurs specifically when the film is more fore-hardened or when the developing solution contains a hardening solution. When the silver content is lowered, the archivability is improved but the overall contrast and the maximum density are too low, so that the image quality becomes inadequate. On the other hand, when the film is developed in a hardener-free developing solution, a sticking and drying problem occurs because of the high silver and gelatine content of the silver halide photographic light sensitive mammographic materials. Lowering the silver content solves this problem, but again the overall contrast and the maximum density are too low, so that the image quality becomes inadequate. Lowering the gelatine content improves the drying characteristics, but physical properties such as roller pressure marks are deteriorated. Decreasing processing time is possible when using X-ray materials that have been adequately fore-hardened so that they absorb less water and lend themselves to accelerated processing and drying. However increasing the level of fore-hardening usually results in a decrease of the overall contrast and the covering power.

[0009] As referred to above decreasing the processing time is possible by lowering the silver content of the silver halide photographic light sensitive mammographic material, with a disadvantage of a lower overall contrast and a lower maximum density.

[0010] By using silver grains that are smaller than those used hitherto in silver halide photographic light-sensitive

materials for mammographic applications, the desired overall contrast, shoulder contrast and maximum density can be reached because of the higher covering power of those smaller silver grains. A disadvantage of those smaller silver grains is the lower speed of the silver halide photographic light sensitive material. In mammographic applications one must avoid to increase the patient dose. The speed of a novel combination of a silver halide photographic light sensitive material and a radiographic intensifying screen may not be lower than that of the combinations that are used hitherto in mammographic applications.

3. Objects of the invention.

[0011] Therefore it is an object of this invention to provide a screen-film image-forming system wherein a light-sensitive silver halide photographic material for mammography is used having smaller silver halide grains than conventionally, in combination with an intensifying screen in order to obtain a very high image quality, i.e., low fog level, high toe contrast and overall-contrast with an enhanced sharpness.

[0012] It is another object of this invention to provide a screen-film image-forming system with a light-sensitive silver halide photographic material showing a characteristic curve and an image quality, that is substantially unaffected by the processing conditions, after being exposed to light emitted from an X-ray intensifying screen.

[0013] It is a further object of this invention to provide a screen-film image-forming system wherein the light-sensitive silver halide photographic material is suitable for rapid processing within cycles of 45 and 38 seconds, without loss in image quality or sensitivity, and with good archival characteristics.

[0014] Other objects will become apparent from the description, given hereinafter.

4. Summary of the invention.

[0015] In accordance with the present invention the above objects are accomplished by providing an image-forming system for mammography consisting of an X-ray photographic light-sensitive silver halide film material comprising a support and one or more hydrophilic colloid layers including on one side of the support only in at least one layer spectrally sensitised gold and sulphur, selenium or tellurium sensitised monodisperse cubic silver bromide or silver bromiodide grains with a mean crystal diameter of between 0.1 and 0.8 μm in an amount corresponding to at least 4 g of silver nitrate per sq.m., the amount of metallic gold, corresponding to the amount of gold compound used in the chemical ripening, relative to the amount of metallic silver, corresponding to the amount of silver halide coated being in the range of 25 to 45 ppm; in operative association with an intensifying screen comprising on a support at least one layer of a green-light emitting phosphor in a coating amount-of at least 45 mg/cm² and the phosphor to binder ratio being at least 97:3.

5. Detailed description.

[0016] In accordance with this invention it has been found that especially silver bromide and silver bromiodide emulsions with cubic crystal habit are showing favourable development characteristics with respect to high image quality, without the risk of high fog densities, if the said emulsions are chemically sensitized with high amounts of gold sensitizer. Normally it would be expected to base a screen-film system for mammography on tabular grains for obtaining maximum image quality.

[0017] Even if the said emulsions with cubic crystal habit are in addition showing reduction sensitization due to low pAg values maintained during the precipitation and/or during the chemical ripening stage and (100)-crystal faces are particularly sensitive to fog the sensitivity to fog enhancement is suppressed by the large amounts of gold compounds.

[0018] The parameter determining whether cubic crystals are formed during the precipitation stage of the photographic emulsion making is the pAg of the solution. The pAg of the solution may be regulated by any of the means known in the art of emulsion making, such as the electronic control apparatus and method disclosed in US-P 3,821,002.

[0019] From the article "Der Einfluß der Wachstumsbedingungen auf die Kristalltracht der Silberhalogenide" (the influence of Growth Conditions on the Crystalline Behaviour of Silver halides) von E.Moisar and E.Klein, Bunsengesellschaft für physikalische Chemie, Berichte 67 949-957 (1963) No 9.10., it is known that on allowing tetradecahedral crystals of a homodisperse silver bromide emulsion to grow by controlled addition of solutions of AgNO₃ and KBr, crystals of cubic form are obtained under conditions of low excess bromide concentration in the solution phase. With increasing excess of bromide, (111) surfaces are preferentially developed, and ultimately pure octahedral growth is observed.

[0020] The pAg-values yielding cubic, resp. octahedral crystals depend on the temperature. In Table I the pAg-neutrality values are set forth for various temperatures, as well as the values for the formation of cubic and octahedral crystals respectively at these temperatures, which are above the pAg-neutrality values.

[0021] The last column gives the 'change-over pAg values', i.e. the pAg values below which cubic crystals and above

which octahedral crystal formation is taking place. Around these pAg values the crystal formation balances between the cubic and the octahedral structure. Values for pAg-neutrality and those preferred for cubic or octahedral crystal formation are summarized in Table I.

Table I

Temp. (°C)	pAg neutrality	formation pAg for cubic crystals	formation pAg for octahedral crystals	Change-over pAg-value: cubes to octaeders
80°C	5.0	6.5	8.8	8.1
60°C	5.4	7.0	9.4	8.7
40°C	5.8	7.5	10.1	9.2
20°C	6.3	8.0	10.9	9.9

[0022] From the above table it is apparent that the cubic silver halide emulsions as used in the film-screen system according to the present invention are precipitated generally under pAg conditions between 6.5 and 8.0.

[0023] The silver halide emulsions formed comprise silver bromide or silver bromiodide. Preferred silver bromiodide emulsions comprise at most 10 mole% of iodide, more preferably at most 3 mole% and more preferably at most 1 mole%.

[0024] A preferred embodiment of making the emulsions used in the film-screen system according to the present invention involves the preparation of high-sensitive silver bromide or silver bromiodide emulsions by precipitation under balanced double jet conditions.

[0025] The average grain-size of the silver halide emulsions made for use in the system according to the present invention is between 0.1 and 0.8 μm and more preferably between 0.2 and 0.5 μm . Grain-growth restrainers or accelerators may be used during the precipitation, and the flow rate and concentration of the solutions, the temperature, pAg etc. may be varied to obtain the desired particle size of the silver halide grains. The said particle size can be determined using conventional techniques e.g. as described by Trivelli and M. Smith, The Photographic Journal, vol. 69, 1939, p. 330-338, Loveland "ASTM symposium on light microscopy" 1953, p. 94-122 and Mees and James "The Theory of the photographic process" (1977), Chapter II.

[0026] Monodispersed emulsions for use in the system according to the present invention are prepared depending on the initial conditions during precipitation. Monodispersed emulsions are characterized in the art as emulsions of which at least 95 % by weight or number of the grains have a diameter which is within about 40 %, preferably within about 30 % of the mean grain-diameter and more preferably within about 10% to 20%. A preferred variation coefficient for emulsion grains for use in the system according to this invention has a value of .25, more preferred between .15 and .20, and still more preferred of .10, said variation coefficient being defined as the ratio between the standard deviation of the grain size and the mean crystal size.

[0027] Silver halide grains having a narrow grain-size distribution can be obtained by controlling the conditions at which the silver halide grains are prepared using a double jet procedure. In such a procedure, the silver halide grains are prepared by simultaneously running an aqueous solution of a water-soluble silver salt for example, silver nitrate, and water soluble halide, for example, potassium bromide, into a rapidly agitated aqueous solution of a silver halide peptizer, preferably gelatin, a gelatin derivative or some other protein peptizer. Even colloidal silica may be used as a protective colloid as has been described in EP-A- 392 092. In order to prepare silver bromide or silver bromiodide crystals having a predictable size in colloidal silica as a protective colloid, the disclosure in EP-A- 649 051, has to be considered.

[0028] In a preferred embodiment the rates of addition of the silver nitrate and halide salt solutions are steadily increased in such a way that no renucleation appears in the reaction vessel. This procedure is especially recommended, not only to save time but also to avoid physical ripening of the silver halide crystals during precipitation, the so-called Ostwald ripening, which gives rise to the broadening of the silver halide crystal distribution. During the precipitation the volume present in the vessel may be reduced making use of ultrafiltration techniques, which may be further applied to remove the by-products of grain-formation and grain-growth once the grains have reached their ultimate size and shape. Demineralized water, or water with a constant amount of halide salts to wash the ultrafiltrated emulsion to a desired pAg value, may be used, wherein the amounts of water may be added continuously or in portions.

[0029] In accordance with the present invention, the emulsions for use in the film, making part of the system, are preferably washed by acid-coagulation techniques using acid-coagulable gelatin derivatives or anionic polymeric compounds or, when precipitation occurred in silica medium, by certain polymers capable of forming hydrogen bridges with silica, in an amount sufficient to form coagulable aggregates with the silica particles as has been described in EP-A 517 961 and 704 749.

[0030] Coagulation techniques using acid-coagulable gelatin derivatives have been described e.g. in U.S. Patents 2,614,928, 2,614,929 and 2,728,662. The acid-coagulable gelatin derivatives are reaction products of gelatin with organic carboxylic or sulphonic acid chlorides, carboxylic acid anhydrides, aromatic isocyanates or 1,4-diketones. The use of these acid-coagulable gelatin derivatives generally comprises precipitating the silver halide grains in an aqueous solution of the acid coagulable gelatin derivative or in an aqueous solution of gelatin to which an acid coagulable gelatin derivative has been added in sufficient proportion to impart acid-coagulable properties to the entire mass. Alternatively, the gelatin derivative may be added after the stage of emulsification in normal gelatin, and even after the physical ripening stage, provided it is added in an amount sufficient to render the whole coagulable under acid conditions. Examples of acid-coagulable gelatin derivatives suitable for use in accordance with the present invention can be found, e.g., in the USP's referred to above. Particularly suitable are phthaloyl gelatin and N-phenyl carbamoyl gelatin.

[0031] It is also possible to wash the emulsion by coagulation techniques using anionic polymeric compounds. Such techniques have been described e.g. in German Patent DE 1,085,422. Particularly suitable anionic polymeric compounds are polystyrene sulphonic acid and sulphonated copolymers of styrene. The anionic polymers can be added to the gelatin solution before precipitation of the silver halide grains or after the stage of emulsification. They are preferably added after the grains have reached their ultimate size and shape, i.e. just before washing. It is also possible to use anionic polymers in combination with acid-coagulable gelatin derivatives as described in the published German Patent Specification No. 2,337,172 (DOS). It is preferred to use low-molecular weight polystyrene sulphonic acid having a molecular weight of at most 30,000. The polystyrene sulphonic acid can be added to the gelatin solution from aqueous solutions preferably comprising from 5 to 20 % by weight of polystyrene sulphonic acid. The amounts used suffice to impart coagulation properties to the emulsion and can easily be determined by those skilled in the art.

[0032] After the precipitation stage, the silver halide emulsion comprising acid-coagulable gelatin derivative or anionic polymer is acidified e.g. by means of dilute sulphuric acid, citric acid, acetic acid, etc. so as to effect coagulation. Coagulation generally occurs at a pH value comprised between 3 and 4. The coagulum formed may be removed from the liquid by any suitable means, for example the supernatant liquid is decanted or removed by means of a siphon, whereupon the coagulum is washed out once or several times.

[0033] Washing of the coagulum may occur by rinsing with mere cold water. However, the first wash water is preferably acidified to lower the pH of the water to the pH of the coagulation point. Anionic polymer e.g. polystyrene sulphonic acid may be added to the wash water even when an acid coagulable gelatin derivative has been used e.g. as described in published German Patent Specification (DOS) 2,337,172 mentioned hereinbefore. Alternatively washing may be effected by redispersing the coagulum in water at elevated temperature using a small amount of alkali, e.g. sodium or ammonium hydroxide, re-coagulating by addition of an acid to reduce the pH to the coagulation point and subsequently removing the supernatant liquid. This redispersion and re-coagulation operation may be repeated as many times as is necessary.

[0034] After the washing operation, the coagulum is redispersed to form a photographic emulsion suitable for the subsequent finishing and coating operations by treating, preferably at a temperature within the range of 35 to 70°C, with the required quantity of water, normal gelatin and, if necessary, alkali for a time sufficient to effect a complete redispersal of the coagulum.

[0035] Instead of or in addition to normal gelatin, which is preferably used, other known photographic hydrophilic colloids can also be used for redispersion e.g. a gelatin derivative as referred to above, albumin, agar-agar, sodium alginate, hydrolysed cellulose esters, polyvinyl alcohol, hydrophilic polyvinyl copolymers, colloidal silica etc.

[0036] In accordance with the present invention the light-sensitive silver bromide or silver bromiodide emulsions are chemically sensitized with a sulphur, selenium or tellurium and gold sensitizer. This can be done as described i.a. in "Chimie et Physique Photographique" by P. Glaftides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature sulphur sensitization 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.

[0037] Gold sensitization occurs by means of gold compounds, e.g. gold chloride. The addition of thiocyanate ions to the gold ion containing solution is highly preferred so that the gold compound is partially or totally replaced by a gold thiocyanate complex ion that is added as such to the emulsion containing vessel wherein the chemical sensitization is carried out.

[0038] It is highly preferred in the system in accordance with this invention to add to the emulsion an amount of gold compound in the range from 25 ppm of metallic gold to 45 ppm vs. the amount of metallic silver, corresponding with the amount of silver halide coated. In a preferred embodiment the amount of gold as described hereinbefore is preferably in the range of 30 to 40 ppm.

[0039] Additions of sulphur and/or selenium and/or tellurium and gold may be carried out consecutively or simultaneously. In the latter case the addition of goldthiosulphate, goldselenosulphate or goldtellurosulphate compounds may

be recommended.

[0040] In a preferred embodiment in accordance with this invention the weight ratio between added amounts of sulphur, selenium or tellurium and of gold sensitizer is situated between 0.5 and 5.0 and more preferably between 0.5 and 2.0.

[0041] In addition small amounts of compounds of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd or Pt may be used. The emulsions may be sensitized in addition by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds.

[0042] Pretreatment with small amounts of oxidizing agents before adding the already mentioned chemical sensitizers is highly preferred in order to optimize the attainable fog to sensitivity relationship.

[0043] In accordance with the present invention compounds for use in the film-screen system for preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof may be added. Examples of such stabilizers are heterocyclic nitrogen-containing stabilizing compounds as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methyl-benzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole, mercaptopyrimidines, mercaptotriazines, benzothiazoline-2-thione, oxazoline-thione, triazaindenes, tetrazaindenes and pentazaindenes, especially those described by Birr in Z. Wiss. Phot. 47 (1952), pages 2-58, triazolopyrimidines such as those described in GB-A 1,203,757, GB-A 1,209,146, UP-A-75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US Patent No. 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, benzenethiosulphonic acid amide and other disulfide derivatives, and 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) as described by H. Takiguchi in J.I-mag. Sci., 32(1), 1988, p.20. Besides the addition of 3-pyrazolidinone stabilizing compounds is highly preferred.

[0044] The stabilizing agents mentioned hereinbefore are usually added to the coating compositions, especially to the silver halide emulsion containing coating compositions, although the addition of said stabilizing agents to other hydrophilic compositions may not be excluded in order to improve the storage stability of the photographic material, even in severe circumstances of heat and humidity. So the addition of at least one stabilizer, e.g. 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene and/or 3-pyrazolidinone and/or phenylmercaptotriazole or -tetrazole compounds, to, e.g., the hydrophilic protective layer is highly preferred. Especially the addition of small amounts of at least one of the selected stabilizers mentioned hereinbefore before, during or at the end of the chemical ripening is desirable. The chemical ripening may proceed at high temperatures, e.g., 70°C, but preferably proceeds below 50°C.

[0045] In order to further improve the storage stability of the photographic material in accordance with this invention the temperature at which the chemical ripening proceeds is lower than 50°C and still more preferably lower than 47°C, although this measure may deteriorate the sensitivity of the coated material for darkroom light. In this case a compensation may be found by the addition to the silver halide emulsion of the different chemical ripening agents at higher temperatures, e.g. between 55 and 70°C, followed by quickly decreasing the temperature to the preferred value below 50°C.

[0046] The cubic silver bromide and silver bromiodide emulsions used in the system according to this invention are spectrally sensitized e.g. with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine 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 is given in Research Disclosure Item 22534. Especially preferred green sensitizers in connection with the present invention are anhydro-5,5'-dichloro-3,3'-bis(n,sulfobutyl) -9-ethyloxacarbo-cyanine hydroxide and anhydro-5,5'-dichloro-3,3'-bis(n,sulfopropyl)-9-ethyloxacarbocyanine hydroxide.

[0047] Furthermore, green-light absorbing spectral sensitizers according to the formulae given in JP-A's 06 035 104, 06 035 101, 06 035 102, 62 191 847, 63 249 839, 01 312 536, 03 200 246, US-P's 4,777,125; and DE 3 819 241 may be used. The right choice of said sensitizers or combinations thereof is always related with the purpose to reduce dye stain after processing.

[0048] The binders of the photographic element, especially when the binder used is gelatin, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, di-(vinyl-sulphonyl)-methane or ethylene di-(vinyl-sulphone), the last two vinyl sulphonyl compounds being preferred ones, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucosalogenics acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binders can also be hardened

with fast-reacting hardeners such as carbamoylpyridinium salts.

[0049] The photographic element for use in the system of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, siliconepolyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulphy, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g. higher contrast, sensitization, and development acceleration.

[0050] Especially from the viewpoint of rapid processing conditions development acceleration may be useful, which can be accomplished with the aid of various compounds, preferably polyoxyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805 - 4,038,075 - 4,292,400.

[0051] Especially preferred developing accelerators are recurrent thioether groups containing polyoxyethylenes as described in DE 2 360 878, and later on in EP-A. 634 688 and 674 215 filed respectively July 12, 1993 and March 11, 1994. The same or different or a mixture of different developing accelerators may be added to at least one of the hydrophilic layers at the emulsion side. More preferably at least one development accelerator is added to at least one of the protective layers, preferably to the topcoat layer.

[0052] 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, hardeners, plasticizers, antistatic agents etc...

[0053] Suitable additives for improving the dimensional stability of the photographic element in the system according to this invention are i.a. dispersions of a water-soluble or hardly soluble synthetic polymer e.g. polymers of alkyl (meth)acrylates, alkoxy(meth)acrylates, glycidyl (meth)acrylates, (meth)acrylamides, vinyl esters, acrylonitriles, olefins, and styrenes, or copolymers of the above with acrylic acids, methacrylic acids, α - β -unsaturated dicarboxylic acids, hydroxy-alkyl (meth)acrylates, sulphonyl (meth)acrylates, and styrene sulphonic acids.

[0054] Suitable UV-absorbers are i.a. aryl-substituted benzotriazole compounds as described in US-A 3,533,794, 4-thiazolidone compounds as described in US-A 3,314,794 and 3,352,681, benzophenone compounds as described in JP-A 2784/71, cinnamic ester compounds as described in US-A 3,705,805 and 3,707,375, butadiene compounds as described in US-A 4,045,229, and benzoxazole compounds as described in US-A 3,700,455.

[0055] In general, the average particle size of spacing agents is comprised between 0.2 and 10 μ m. 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 i.a. of polymethyl methacrylate, of copolymers of acrylic acid and methyl methacrylate, and of hydroxypropylmethyl cellulose hexahydrophthalate. Other suitable spacing agents have been described in US-A 4,614,708.

[0056] The photographic material used in the system in accordance with this invention is preferably composed of at least one silver halide emulsion layer and at least one hydrophilic layer coated thereover, useful as a protective layer. Besides an afterlayer may be coated as an outermost layer.

[0057] The said at least one silver halide emulsion layer may comprise at least one silver halide emulsion comprising silver bromide or silver bromiodide crystals as described hereinbefore. Mixtures of silver halide crystals having the same crystal size but being chemically sensitized differently or mixtures of crystals of a different crystal size may be used in at least one layer. Otherwise, silver halide emulsion crystals of the same size may be added to different silver halide emulsion layers, said silver halide emulsion crystals being chemically ripened with different amounts of ripening agents or silver halide crystals of a different size may be coated into different emulsion layers.

[0058] In accordance with this invention the coated amounts of the silver bromide and/or silver bromiodide emulsion crystals in the emulsion layer(s) of the light-sensitive film material making part of the system are preferably amounts corresponding to about 4.0 to 8.5 g/m² of AgNO₃. More preferably amounts corresponding to from 5.0 to 7.0 g/m² of AgNO₃ are coated in order to enhance the utility in rapid processing conditions within 45, resp. 38 seconds, especially from the viewpoint of archivability, to be understood is a complete fixation by removal of any excess of unexposed silver halide.

[0059] In a preferred embodiment only one silver halide emulsion layer is coated onto the support, having a substrate layer to provide good adhesion characteristics, which emulsion layer is overcoated with a protective antistress layer.

[0060] Preferred compounds present in the silver brom(iod)ide emulsion layer in the system according to this invention and in the protective layer coated onto the silver halide emulsion layer will be illustrated in the examples following further on.

[0061] The photographic element may comprise an antistatic layer e.g. to avoid static discharges during coating, processing and other handlings of the material. Such antistatic layer may be an outermost coating, like the protective layer or an afterlayer, or a stratum of one or more antistatic agents or a coating applied directly to the film support or other support and overcoated with a barrier or gelatin layer. Antistatic compounds suitable for use in such layers are e.g. vanadium pentoxide sols, tin oxide sols or conductive polymers such as polyethylene oxides or a polymer latex and the like.

[0062] In accordance with this invention the silver bromide or silver bromiodide emulsions coated in the emulsion layer(s) of the film material making part of the system do reveal a low fog level, a high gradation, especially at low densities, and an excellent developability in different processing conditions. They are particularly suitable for rapid processing applications, especially in processing cycles of 45 and even 38 s. Besides the opportunity is offered to fine-tune the gradation by lowering the coated amount of silver halide crystals and/or enhancing the hardening degree of the hydrophilic binders. The said enhancement of the hardening degree of the coated material provides the possibility to use hardener free processing solutions. This opens the way to one-part package chemistry and concentration regeneration, reducing the volume of chemicals and the amount of packaging material, which is highly requested from the point of view of ecology.

[0063] Further lowering the coated amount of silver halide crystals is in favour of archivability due to a higher fixation capacity, whereas an enhanced hardening degree is in favour of a lower water absorption and a higher drying capacity in the processing, avoiding sticking phenomena. Lower amounts of coated silver halide crystals that are causing less scattering from the incident light radiating from the intensifying screen during exposure and the high gradations observed after processing are two important factors in favour of the high definition of the obtained images, enhancing its diagnostic value.

[0064] In the screen/film image-forming system disclosed in this invention the features of the intensifying screen emitting green light are at least as important as the features offered by the silver halide photographic material used in this system. Image quality, i.e., granularity and sharpness are measured at the processed silver halide photographic film that is used in combination with the said intensifying screen. More in detail it is well-known that sharper images are obtained with phosphor particles of smaller mean particle size, but light emission efficiency declines with decreasing particle size. Thus, the optimum mean particle size for a given application is a compromise between imaging speed and image sharpness desired.

[0065] The synergistic effect obtained between image speed and image sharpness are, i.e., the coated amount of phosphor, the optional presence of a coloured dye in the said coated phosphor layer and the reflectance of the support on which the phosphor layer was coated.

[0066] A preferred phosphor coated in the intensifying screen for use according to this invention is $\text{Gd}_2\text{O}_2\text{S:Tb}$. Said phosphor and the use in intensifying screens has been described e.g. in US-P's 3,872,309; 4, 130,429; 4,912,333; 4,925,594; 4,994,355; 5,021,327; 5,107,125 and 5,259,016 and in GB 1,489,398.

[0067] As is well-known the thickness of the phosphor layer may differ depending on the amount of phosphor used. Usually said thickness is within the range of from 50 to 1000 μm , preferably from 50 to 500 μm and more preferably from 150 to 250 μm .

[0068] The coated amounts of phosphor(s) vary depending on the desired screen speed. For screens used in the film-screen system according to this invention the amounts of phosphor, expressed in mg/cm^2 , are at least 45 mg per sq.m. and more preferably in the range of 50 to 60 mg. A high phosphor screen speed is required in combination with a silver halide photographic material having low speed, due to the fine cubic grains used therein.

[0069] As is well-known radiographic conversion screens for medical diagnostic purposes are coated onto a support. Examples of support materials include cardboard, plastic films such as films of cellulose acetate, polyvinyl chloride, polyvinyl acetate, polyacrylonitrile, polystyrene, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate and polycarbonate; metal sheets such as aluminum foil and aluminum alloy foil; ordinary papers; baryta paper; resin-coated papers; pigment papers containing titanium dioxide; and papers sized with polyvinyl alcohol. A plastic film is preferably employed as the support material.

[0070] Depending on the speed class of the screens for which an optimum relationship has to be attained between speed and sharpness, the supports are chosen as a function of their reflectance properties, expressed as % reflectance over the wavelength range from 350 to 600 nm. Said percentage reflection for each of the support materials was measured with a spectrophotometer from the type PERKIN ELMER 555. So, e.g., barium sulphate is taken as a reference point with a percentage reflectance of 100% within the wavelength region between 350 and 600 nm. A terephthalate support containing carbon black as light-absorbing material is taken as representative for a low percentage reflectance of 0-5%.

[0071] X-ray conversion screens used in the film-screen system in accordance with the present invention generally

comprise in order: a support (also called substrate), preferably a reflective or a specular reflective support, at least one layer comprising phosphor particles dispersed in a suitable binder and a protective coating coated over the phosphor containing layer to protect said layer during use. A preferred specular reflected layer is obtained by coating a layer of aluminum onto the support. Said layer can be coated, making use of different coating techniques, preferably a vacuum depositing technique. Further, a primer layer is preferably provided between the phosphor containing layer or the preferred specular reflective layer and the substrate to closely bond said layer thereto. In the preparation of the phosphor screen having a primer layer between the substrate and the fluorescent layer, the primer layer is provided on the substrate beforehand, and then the phosphor dispersion is applied to the primer layer and dried to form the fluorescent layer. Especially suited for the screen used in the film-screen system according to this invention, is a primer layer which has high solvent resistivity, e.g., a cross-linked primer layer with di- or tri-isocyanate with a polyester combination. Preferably between said specular reflective layer, being preferably an aluminum layer, and said primer layer is a moisture resistant layer. Said moisture resistant layer is a synthetic resin layer, which preferably contains silica.

[0072] In most applications the phosphor layers contain sufficient binder to give structural coherence to the layer. In view of a possible phosphor recovery from worn-out screens the binder of the phosphor containing layer is preferably soluble and remains soluble after coating.

[0073] Useful binders, a non-limitative survey of which is given herein, include proteinaceous binders, e.g. gelatin, polysaccharides such as dextran, gum arabic, and synthetic polymers such as polyvinyl butyral, polyvinyl acetate, nitrocellulose, ethylcellulose, vinylidene chloride-vinyl chloride copolymer, polyalkyl (meth)acrylate, vinyl chloride-vinyl acetate copolymer, polyurethane, cellulose acetate, cellulose acetate butyrate, polyvinyl alcohol, polystyrene, polyester, etc. These and other useful binders are disclosed e.g. in US-P's 2,502,529; 2,887,379; 3,617,285; 3,300,310; 3,300,311 and 3,743,833.

[0074] Also suited as a binder system is the mixture of known binders with a so-called dispersing resin. For example "Disperse Ayd 9100" which is a modified thermoplastic acrylic polymer which has binder as well as dispersing properties and is a trademarked product from Daniel Products Company, New Jersey, USA.

[0075] A mixture of two or more of these binders may be used, e.g., a mixture of polyethyl acrylate and cellulose acetobutyrate.

[0076] In the prior art the weight ratio of phosphor to binder is generally within the range of from 50:50 to 99:1, preferably from 90:10 to 99:1. In the present invention the ratio is at least 97:3.

[0077] The screen useful in the present invention may comprise a supported layer of phosphor particles dispersed in a binding medium comprising one or more rubbery and/or elastomeric polymers as described in PCT-Application WO-A-94/00530 and WO-A-94/00531, filed on June 17, 1993. In this way a ratio by weight of pigment to binding medium of more than 90:10 and more preferably of at least 95:5, e.g. 98:2 can be obtained providing besides an excellent image resolution a high ease of manipulation as a result of a good elasticity of the screen and good adhesion properties between the support and the phosphor layer. Problems concerning staining of screens comprising said rubbery binder (s) may be overcome by the addition of known rubber anti-oxidation compounds like IRGANOX 1010 and IRGASTAB T36 (trademarked products of CIBA-GEIGY, Basel, Switzerland), ANTIOXIDANT 330 (trademarked product of ETHYL CORP., Richmond, USA), VANOX 2246 (trademarked product of VANDERBILT ENERGY CORP., Denver, Canada), this list being non-limitative.

[0078] The phosphor layer can be applied to the support by employing a method such as vapour deposition, sputtering and spraying but is usually applied by the following procedure.

[0079] Phosphor particles and a binder are added to an appropriate solvent as described hereinafter, and are then mixed to prepare a coating dispersion comprising the phosphor particles homogeneously dispersed in the binder solution. Said coating dispersion may further comprise a dispersing agent and plasticizer and filler material as described hereinafter.

[0080] The coating dispersion containing the phosphor particles and the binder is applied uniformly onto the surface of the support to form a layer of the coating dispersion. The coating procedure may proceed according to any conventional method such as doctor blade coating, dip-coating or roll coating.

[0081] After applying the coating dispersion onto the support, the coating dispersion is then heated slowly to dryness so as to complete the formation of a phosphor layer.

[0082] In order to remove as much as possible entrapped air in the phosphor coating composition it can be subjected to an ultra-sonic treatment before coating. The phosphor-binder layer (as described e.g. in US-P 4,059,768) can be calendered to improve the phosphor packing density in the dried layer.

[0083] For the preparation of highly abrasion resistant and chemically resistant phosphor-binder layers the binder is cured. Curing of the binder may proceed photochemically by means of UV radiation or with electron beam (EB) as described e.g. in Research Disclosure December 1977, item 16435 or proceeds purely chemically as described e.g. in US-P 4,508,636. It may also be cured by moisture as described in EP-Application 541 146 A1. Curing may also be performed by heating.

[0084] Useful solvents for the binder of the phosphor containing layer, employable in the preparation of the phosphor

coating dispersion include lower alcohols such as methanol, ethanol, n-propanol and n-butanol; chlorinated hydrocarbons such as methylene chloride and ethylene chloride; ketones such as acetone, butanone, methyl ethyl ketone and methyl isobutyl ketone; esters of lower alcohols with lower aliphatic acids such as methyl acetate, ethyl acetate and butyl acetate; ethers such as dioxane, ethylene glycol monoethylether; methyl glycol; and mixtures of the above-mentioned solvents.

[0085] Useful dispersing agents for the phosphor particles in the coating dispersion to improve the dispersibility of the phosphor particles therein, may contain a variety of additives such as a plasticizer for increasing the bonding between the binder and the phosphor particles in the phosphor layer. Examples of the dispersing agent include ionic and nonionic well-known dispersing agents or combinations thereof, e.g., GAFAC RM 610 (tradename) a polyoxyethylene (20) sorbitan monopalmitate and monolaurate marketed by General Aniline and Film Company (GAF), New York, USA, polymeric surfactants such as the acrylic graft copolymer, PHOSPHOLIPON 90 (tradename) marketed by Nattermann-Phospholipid GmbH, Köln, W. Germany, silane dispersing agents and surfactants e.g. DOW CORNING 190 (tradename) and SILANE Z6040 (tradename) marketed by Dow Corning Corporation, Midland, Michigan, USA or glymo 3-glycidioxypropylmethoxysilane or organosulfate polysilanes, unsaturated p-aminamide salts and high molecular acid esters such as ANTI TERRA U 80 (tradename) marketed by BYK-Chemie GmbH, Wesel, W. Germany, high molecular unsaturated polyesters, etc. Dispersing agents are added in an amount of 0.05 to 10 % by weight based on the phosphor.

[0086] Useful plasticizers include phosphates such as triphenyl phosphate, tricresyl phosphate and diphenyl phosphate; phthalates such as diethyl phthalate and dimethoxyethyl phthalate; glycolates such as ethylphthalyl ethyl glycolate and butylphthalyl butyl glycolate; polymeric plastizers, e.g. and polyesters of polyethylene glycols with aliphatic dicarboxylic acids such as polyester of triethylene glycol with adipic acid and polyester of diethylene glycol with succinic acid.

[0087] After the formation of the fluorescent layer, a protective layer is generally provided on top of the fluorescent layer.

[0088] In a preferred embodiment the protective coating has a layer thickness d comprised between 1 and 50 μm and an embossed surface roughness is applied for high ease of manipulation, thereby avoiding sticking, friction and electrostatic attraction with maintenance of an excellent image resolution.

[0089] The embossed protective layer can be provided on the phosphor layer in order to protect it against mechanical and chemical damage by the steps of (1) coating onto said phosphor containing layer a liquid radiation-curable composition having at the coating temperature a viscosity of at least 450 mPa.s, measured with a Hoesppler viscometer, that does not penetrate for a substantial degree into the phosphor containing layer, (2) providing an embossed structure to the coating, and (3) curing said coating by radiation.

[0090] For more details concerning preferred protective coatings with embossed surface there is referred to EP-Applications 510 753 A1 and 510 754 A1.

[0091] In a particular embodiment of the present invention the screens are used in combination with a radiographic film material that is provided on one side of the film support with a silver halide emulsion layer and an antistress layer as a protective layer coated thereover. The radiographic material may have on said one side of the film support a silver halide emulsion coating that is split into two distinctive emulsion layers having silver halide crystals of different average grain size one of which is an emulsion layer containing crystals having a higher speed and the other containing crystals having a lower speed; the higher speed emulsion layer being situated at a larger distance from the support than the lower speed emulsion layer. Differences in sensitivity can be obtained, not only by using two emulsions having both a cubic shape, that are differing in crystal size, but also by using different amounts of spectral sensitiser(s) or by chemically ripening the crystals to a different degree, especially if the emulsions used in both layers are identical. Even a differing stabilisation can be used and combinations of the different methods described shortly hereinbefore can be combined as well. This way the sensitometric curve can be fine-tuned giving the perfect required profile after processing in accordance with the methods described hereinbefore.

[0092] With the present film-screen combination an improvement in the speed:image-sharpness relationship can thus be realized.

[0093] The favourable relationship of speed:image-sharpness:granularity will be illustrated in the Examples given hereinafter, without however limiting this invention thereto.

6. Examples.

Example 1Emulsion A

[0094] A chemically sensitized monodisperse negative working silver bromiodide emulsion having a iodide content of 1 mole % was prepared in the following manner.

[0095] 50 g of gelatin were added to 1.000 ml of demineralized water containing 15 g of methionin as a growth accelerator under constant stirring at 400 rpm. The mixture was held for 30 minutes at room temperature and heated up to 60°C. This temperature was kept constant during the entire precipitation process.

[0096] Before starting the precipitation a few drops of a diluted solution of potassium bromide were added so as to bring the pAg of the solution at a value of 7.9.

[0097] 36.5 ml of 2.94 N AgNO₃ (3.65 % of the total amount of AgNO₃) were added under the following conditions. During the first five minutes the flow rate of AgNO₃ was kept constant at 7.3 ml/min. A mixture of 99 % KBr and 1 % KI was added at a variable flow rate so as to keep the pAg constant at 7.9. During the following 68 minutes the flow rate of AgNO₃ was steadily increased from 7.3 ml/min up to 21 ml/min whereas the pAg was kept constant at 7.9 by regulating the flow rate of the mixture of KBr and KI, allowing 963 ml of AgNO₃ to be added. The latter was realised by means of an automated electronic control apparatus for silver halide preparation disclosed by Claes and Peelaers in Photographische Korrespondenz 102, Band Nr. 10/1967, p. 162.

[0098] After five minutes the pH of the emulsion was reduced from 5.8 to 3.5 by adding a sufficient quantity of 6N of sulfuric acid.

[0099] Hereupon the conventional treatment processes such as washing and redispersing were applied to the emulsion: pAg was adjusted to a value of 8.4 at 45°C, pH to a value of 5.8. All of the obtained silver halide crystals had a cubic crystal habit and an average diameter of 0.64 µm was measured.

[0100] The emulsion was chemically sensitized for a period of 4 hours at 48°C in the presence of p-toluene thiosulphonate, sodium thiosulphate, sodium sulphite and of a mixture of gold(III)-chloride and ammoniumthiocyanate. A total amount of gold of 30 ppm with respect to the amount of metallic silver was used.

[0101] The emulsion was spectrally sensitized with anhydro-5,5'-dichloro-3,3'-bis(n.sulfobutyl)-9-ethyloxacarbo-cyanine hydroxide and stabilized with 4-hydroxy-6-methyl-1,3,3a-tetrazaindene before being coated on a polyester support of 175 µm thickness. The emulsion layer was coated with silver halide crystals at a ratio of 6.8g/m² expressed as the equivalent amount of AgNO₃.

[0102] A photographic material was made by coating the emulsion on a polyethylene terephthalate support together with a composition for forming a protective gelatin layer. The amount of gelatin per square meter in the emulsion layer was 3.0 g, whereas in the protective layer it was 1.1 g.

[0103] The screens (comparative screen A and screens B and C, according to this invention) were prepared in the following way.

[0104] The phosphor coating composition A (comparative) was prepared by intimately mixing the following components :

Gd ₂ O ₂ S	100 g
(phosphor; type 3010-18a; average grain size: Nichia Chemical Industries)	3.5 µm;
cellulose acetobutyrate (type 381/2; Eastman Chemical)	3.01 g
polyethyl acrylate (30 % in ethyl acetate) (Plexisol P372; Röhm GmbH; Darmstadt Germany)	4.52 g
ethyl acetate	20 g
2-butanone	16 g
dispersing agent GAFAC RM 610 (tradename)	0.5 g

[0105] Screen A was coated on a terephthalate support containing carbon black as light-absorbing material having a low percentage reflectance of 0-5%.

[0106] In the said screen the ratio of phosphor to binder was 93:7; the coating amount of the phosphor was 40 mg/cm².

[0107] The phosphor coating composition B (invention) was prepared by intimately mixing the following components :

Gd ₂ O ₂ S	100 g
binder (KRATON 1901X; trademarked product from SHELL)	3.09 g
toluene	20 g

(continued)

dispersing agent DISPERSE AYD (DANIEL PRODUCTS COMPANY NEW JERSEY USA)	0.25 g
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[0108] Screen B was coated on a terephthalate support containing carbon black as light-absorbing material having a low percentage reflectance of 0-5%, just as for screen A.

[0109] In the said screen B the ratio of phosphor to binder was 97:3; the coating amount of the phosphor was 56 mg/cm².

[0110] The composition of screen C is given hereinafter:

Screen C

[0111]

Gd ₂ O ₂ S	100 g
binder (KRATON 1901X; trademarked product from SHELL)	3.09 g
toluene	20 g
dispersing agent DISPERSE AYD (DANIEL PRODUCTS COMPANY NEW JERSEY USA)	0.25 g

[0112] Screen C was coated on a PET-layer having a vapour deposited aluminum layer. A solvent resistant primer layer is necessary to protect the aluminum layer when coating the phosphor layer. In said screen C the ratio of phosphor to binder was 97/3; the coating amount of the phosphor was 50 mg/cm².

[0113] The single-side coated silver halide photographic film described hereinbefore was brought into contact with the screens A, B and C respectively.

[0114] An X-ray exposure proceeded with 28 kVp X-rays for chest exposure with a filter of 35 mm-plexi at the screen-film system and a FFA of 400 cm dlogK of 0.10. In the curve obtained the density is plotted versus the corrected logK value, wherein said value is corrected for the air absorption.

[0115] The processing of the exposed silver halide emulsion materials, called material A (which was into contact with screen A, being the comparative screen) and materials B and C (which were brought into contact with screen B and screen C respectively, being the screens for use in the system according to this invention) proceeded with the following developing liquid, followed by fixing and rinsing at the indicated temperature and processing time.

[0116] The developing liquid had the following composition:

hydroquinone	30 g
1-phenyl-pyrazolidine-3-one	1.5 g
acetic acid 99 %	9.5 ml
potassiumsulphite	63.7 g
potassiumchloride	0.8 g
EDTA-2Na	2.1 g
potassium carbonate	32 g
potassiummetabisulfite	9 g
potassium hydroxyde	14 g
diethyleneglycol	25 ml
6-methylbenztriazol	0.09 g
glutardialdehyd 50%	9.5 ml
5-nitroindazole	0.25 g
demineralized water to make 1 l.	

[0117] The starter solution to be added had the following composition:

acetic acid 99 %	15.5 ml
KBr	16 g
demineralized water up to 100 ml	

[0118] The overall developing time was 12 seconds at 37 °C in the total processing cycle of 45 seconds. Hereupon, the developed photographic strips were fixed in a conventional fixing bath comprising, ammonium thiosulfate and potassium metabisulfite, and then rinsed in water and allowed to dry.

[0119] Sensitometric properties and values of sharpness and granularity obtained for the film-screen combinations A, B and C are given in Table 1. This table shows the speed values S, calculated from the sensitometric curve by means of the square law in order to determine the dose necessary to get a netto density of 1.0.

[0120] After processing the SWR values used in connection with Table 1 were determined at 1; 2 and 4 line pairs per mm (SWR1, SWR2 and SWR4 respectively). The determination of the SWR value for intensifying screens was performed with the same kVp after a Funk type K 0.01 mm Pb - 8 lp/mm raster, with a FFA of 400 cm dlogK of 0.10.

[0121] The granularity is expressed as σ_D and was measured at densities above and below a netto density value of 1.0. A smaller σ_D value thus means less noise. The same conditions were applied as for the determination of the sensitometric characteristics.

[0122] From Table 1 given hereinafter it can be concluded that by coating a ca. 40 % larger amount of phosphor in screen B versus screen A an increase in speed of ca. 35 % is obtained, corresponding with 0.14 log units.

[0123] Screen C has the same speed, although its phosphor content is 6 mg/cm² lower. This is due to the reflecting aluminum layer present on the PET undercoat layer.

Table 1

Screen	S	SWR1	SWR2	SWR4	σ_D
A (comp.)	0.19	94	88	68	263
B (inv.)	0.33	94	87	66	265
C (inv.)	0.33	93	86	64	268

[0124] Nevertheless the measured sharpness and granularity of both the inventive and the comparative screen in operative contact with the fine grain mammographic film material used in the film-screen combination according to this invention is not negatively influenced.

Example 2

Emulsion B

[0125] A chemically sensitized monodisperse negative working silver bromiodide emulsion having a iodide content of 1 mole % was prepared in the same manner as Emulsion A, except for the flow rate of silver nitrate which was kept constant at 11.1 ml/min. During the following 43 minutes the flow rate of AgNO₃ was steadily increased from 11.1 ml/min up to 30 ml/min. All of the obtained silver halide crystals had a cubic crystal habit and an average diameter of 0.55 μ m was measured.

[0126] The emulsion was chemically sensitized as for Emulsion A and further spectrally sensitized, stabilized and coated in the same way as Emulsion A. The emulsion layer contained 5.5 g/m² of silver halide expressed as the equivalent amount of AgNO₃.

[0127] The emulsion layer, having an amount of gelatin per sq.m. of 2.4 g, was further covered with a protective gelatin layer at a coverage of 1.1 g per sq.m. .

[0128] The screens (comparative screen A and screens according to this invention B and C) were the same as in Example 1.

[0129] The single-side coated silver halide photographic film B obtained as described hereinbefore was brought into contact with the screen A, respectively screens B and C. An X-ray exposure proceeded as described hereinbefore in Example 1.

[0130] The processing of the exposed silver halide emulsion materials, called material A' (which was into contact with screen A, being the comparative screen) and materials B' and C' (which were brought into contact with screen B, and screen C respectively, being the screens for use in the system according to this invention) proceeded with the same developing liquid, followed by fixing and rinsing. In this Example 2, different processing times were applied: a 45 seconds processing cycle as in the foregoing example, with a developing time of 12 seconds and a 90 seconds processing cycle with a developing time of 23 seconds. Both developing steps were carried out at 37°C.

[0131] Sensitometric properties, like speed S, contrast C and maximum density D_{max} obtained for the film-screen combinations A', B' and C' are given in Table 2. A comparison is made with the results obtained for film-screen combination A of Example 1. Moreover the archivability ("Arch") in the most critical processing cycle (45 seconds) is demonstrated in the Table as well the "sticking-test" (again in the 45 seconds processing cycle), indicating if the material

is perfectly dry or not ("Stick").

[0132] Both tests are described further on.

a. Archivability test.

[0133] A sheet of unexposed film of each sample was processed in the 45 seconds processing cycle. A drop of the test solution composed of 10 grams of silver nitrate and of 30 ml of acetic acid (99%) and sufficient distilled water to make 1 liter of solution; was placed on the film.

[0134] After two minutes the excessive solution amount was blot off. The density difference, between the density on the spot where the solution was placed and the density on the strip next to the spot, was measured with a Macbeth TD903 densitometer. This density difference is a measure for the amount of residual thiosulphate in the film. The said density difference, multiplied by 11, is a measure for the amount of thiosulphate (in mg/m²) retained in the film. To ensure a good archivability, this value should not exceed 175.

b. Sticking test.

[0135] The drying characteristics were evaluated as follows: two consecutively processed identical films were brought into contact with each other with their emulsion sides after they left the drying station and a weight of 1 kg was placed onto it for 30 seconds. Drying is satisfactory, if no sticking appears after the films are separated again: this is indicated by evaluation mark "0". If there is some sticking that is not too prohibitive, an evaluation mark "1" is given, and if it is prohibitive then the mark is "2".

Table 2

Screen-film	S	C	Dmax 90"	Dmax 45"	Arch 45"	Stick
A (comp.)	0.19	3.50	3.70	3.00	247	2
A' (inv.)	0.05	3.60	3.80	3.70	33	0
B' (inv.)	0.19	3.60	3.80	3.70	33	0
C' (inv.)	0.19	3.60	3.70	3.70	33	0

[0136] From Table 2 it can be concluded that the combination of film material B, having smaller cubic crystals than material A, together with screen B or C enhances the speed to the desired level (see combinations B' and C'). Moreover the contrast and maximum densities are matching those required to get a film suitable for use in mammography, even in shorter processing cycles (45"). Further on the archivability is very good as well as the drying capacity.

Claims

1. An image-forming system for mammography consisting of an X-ray photographic light-sensitive silver halide film material comprising a support and one or more hydrophilic colloid layers including on one side of the support only in at least one layer spectrally sensitised gold and sulphur, selenium or tellurium sensitised monodisperse cubic silver bromide or silver bromiodide grains with a mean crystal diameter of between 0.1 and 0.8 μm in an amount corresponding to at least 4 g of silver nitrate per sq.m., the amount of metallic gold, corresponding to the amount of gold compound used in the chemical ripening, relative to the amount of metallic silver, corresponding to the amount of silver halide coated being in the range of 25 to 45 ppm; in operative association with an intensifying screen comprising on a support at least one layer of a green-light emitting phosphor in a coating amount of at least 45 mg/cm² and the phosphor to binder ratio being at least 97:3.
2. System according to claim 1, wherein said green-light emitting phosphor is a Gd₂O₂S:Tb phosphor.
3. System according to claim 1 or 2, wherein said emulsion has been sensitized with a gold compound in an amount between 30 and 40 ppm of gold vs. the amount of silver, corresponding to the amount of silver halide coated.
4. System according to any of claims 1 to 3, wherein the mean crystal diameter of the cubic crystals is between 0.2 and 0.5 μm .

5. System according to any of claims 1 to 4, wherein the amount of silver, corresponding to the amount of silver halide coated, is between 4.0 and 8.5 g/m².
6. System according to any of claims 1 to 5, wherein the amount of silver, corresponding to the amount of silver halide coated, is between 5.0 and 7.0 g/m².
7. System according to any of claims 1 to 6, wherein the said film material is hardened with di-(vinyl-sulphonyl)-methane or ethylene di-(vinyl-sulphone).
8. System according to any of claims 1 to 7, wherein said screen has a specular reflective support composed of an undercoat layer and a primer layer, covered with an aluminum layer.
9. System according to claim 8, wherein a moisture resistant layer is positioned between the aluminum layer and the primer layer.
10. System according to claim 9, wherein said moisture resistant layer is a synthetic resin layer.

Patentansprüche

1. Ein bilderzeugendes System für Mammografie, das aus einem lichtempfindlichen fotografischen Silberhalogenid-röntgen-filmmaterial besteht, wobei das Material einen Träger und eine oder mehrere hydrophile Kolloidschichten enthält, wobei auf nur einer Seite des Trägers wenigstens eine Schicht mit Gold und Schwefel, Selen oder Tellur sensibilisierte und spektral sensibilisierte mono-disperse kubische Silberbromid- oder Silberbromidiodidkörner mit einem mittleren Kristalldurchmesser zwischen 0,1 und 0,8 µm in einer Menge entsprechend wenigstens 4 g Silbernitrat/m² enthält, wobei die der bei der chemischen Reifung verwendeten Menge Goldverbindung entsprechende Menge Metallgold, bezogen auf die der Menge aufgetragenen Silberhalogenids entsprechende Menge Metallsilber, zwischen 25 und 45 ppm liegt, und zwar in wirksamer Beziehung zu einem Verstärkerschirm, der auf einem Träger wenigstens eine Schicht aus einem Grünlicht emittierenden Leuchtstoff in einer Gießmenge von 45 mg/cm² mit einem Leuchtstoff-Bindemittel-Verhältnis von wenigstens 97:3 enthält.
2. System nach Anspruch 1, dadurch gekennzeichnet, daß der Grünlicht emittierende Leuchtstoff ein Gd₂O₂S:Tb-Leuchtstoff ist.
3. System nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Emulsion in einer Menge zwischen 30 und 40 ppm Gold, bezogen auf die der Menge aufgetragenen Silberhalogenids entsprechende Silbermenge, mit einer Goldverbindung sensibilisiert ist.
4. System nach irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der mittlere Kristalldurchmesser der kubischen Kristalle zwischen 0,2 und 0,5 µm liegt.
5. System nach irgendeinem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die der Menge aufgetragenen Silberhalogenids entsprechende Silbermenge zwischen 4,0 und 8,5 g/m² liegt.
6. System nach irgendeinem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die der Menge aufgetragenen Silberhalogenids entsprechende Silbermenge zwischen 5,0 und 7,0 g/m² liegt.
7. System nach irgendeinem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Filmmaterial mit Di-(vinylsulfonyl)-methan oder Ethylendi-(vinylsulfon) gehärtet ist.
8. System nach irgendeinem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Schirm einen spiegelnden Träger, der aus einer Trägerschicht und einer mit einer Aluminiumschicht überzogenen Grundierschicht besteht, umfaßt.
9. System nach Anspruch 8, dadurch gekennzeichnet, daß zwischen der Aluminiumschicht und der Grundierschicht eine feuchtigkeitsbeständige Schicht eingefügt ist.
10. System nach Anspruch 9, dadurch gekennzeichnet, daß die feuchtigkeitsbeständige Schicht eine synthetische

Harzschicht ist.

Revendications

1. Un système formateur d'image pour la mammographie, composé d'un matériau radiographique de film photographique à l'halogénure d'argent photosensible comprenant un support et une ou plusieurs couches colloïdales hydrophiles, renfermant sur un côté du support dans au moins une couche des grains monodispersés cubiques de bromure d'argent ou de bromo-iodure d'argent sensibilisés spectralement et sensibilisés à l'or et au soufre, au sélénium ou au tellurium, avec un diamètre moyen du cristal entre 0,1 et 0,8 μm , dans une quantité correspondant à au moins 4 g de nitrate d'argent par mètre carré, où la quantité d'or métallique, correspondant à la quantité du composé d'or utilisé dans la maturation chimique, par rapport à la quantité d'argent métallique, correspondant à la quantité d'halogénure d'argent coulée, se situe entre 25 et 45 ppm; en relation opérante avec un écran renforçateur comprenant sur un support au moins une couche d'un luminophore émettant de la lumière verte dans un taux d'enduction d'au moins 45 mg/cm^2 , avec un rapport luminophore/liant d'au moins 97:3.
2. Système selon la revendication 1, caractérisé en ce que le luminophore émettant de la lumière verte est un luminophore $\text{Gd}_2\text{O}_2\text{S:Tb}$.
3. Système selon la revendication 1 ou 2, caractérisé en ce que l'émulsion a été sensibilisée avec un composé d'or dans une quantité entre 30 et 40 ppm d'or versus la quantité d'argent correspondant à la quantité d'halogénure d'argent coulée.
4. Système selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le diamètre moyen des cristaux cubiques est entre 0,2 et 0,5 μm .
5. Système selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la quantité d'argent, correspondant à la quantité d'halogénure d'argent coulée, est entre 4,0 et 8,5 g/m^2 .
6. Système selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la quantité d'argent, correspondant à la quantité d'halogénure d'argent coulée, est entre 5,0 et 7,0 g/m^2 .
7. Système selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le matériau de film est durci au di(vinylsulfonyl)méthane ou à l'éthylène-di(vinylsulfone).
8. Système selon l'une quelconque des revendications 1 à 7, caractérisé en ce que l'écran a un support réfléchissant spéculaire composé d'une sous-couche et d'une couche de fond, enduit d'une couche d'aluminium.
9. Système selon la revendication 8, caractérisé en ce que une couche résistante à l'humidité est positionnée entre la couche d'aluminium et la couche de fond.
10. Système selon la revendication 9, caractérisé en ce que la couche résistante à l'humidité est une couche de résine synthétique.