

PATENT SPECIFICATION (11) 1 591 610

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(21) Application No. 41752/76 (22) Filed 7 Oct. 1976

(23) Complete Specification Filed 13 Sep. 1977

(44) Complete Specification Published 24 Jun. 1981

(51) INT. CL.³ G03C 1/02

(52) Index at Acceptance
G2C C19FX C19G5
G2X B29

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(54) RAPIDLY PROCESSABLE RADIOGRAPHIC MATERIAL

(71) We, AGFA-GEVAERT, a naamloze vennootschap organised under the laws of Belgium, of Septestraat 27, B 2510 Mortsel, Belgium do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

5 The present invention relates to rapidly processable radiographic silver halide material and especially to rapidly processable radiographic material for direct exposure (i.e. without the aid of fluorescent screens) to penetrating radiation e.g. industrial material for non-destructive testing and medical radiographic material e.g. for use in mammography.

10 It is known that the overall sensitivity of silver halide emulsions increases with increasing grain-size and that highest sensitivity is reached with silver halide emulsions the halide of which consists substantially of bromide. Therefore it is common practice to employ for recording X-ray exposures relatively coarse-grained emulsions more particularly ammoniacal silver bromide emulsions, which may contain minor amounts of iodide and chloride as mixed halides.

15 It is also known that the silver halide grains of conventional photographic emulsions are sensitive to radiation both on the surface and internally. The primitive emulsions i.e. the emulsions before any chemical sensitization has taken place, not only have a poor overall sensitivity but their internal sensitivity generally surpasses the surface sensitivity. In most types of photographic processes, however, the surface sensitivity is more important than the internal sensitivity because normally surface developers are used, which contain little or no solvent for silver halides and which react only or predominantly with those latent image specks situated at or near the surface of the silver halide grains.

20 A high surface sensitivity is beneficial for recording of all types of exposures but most of all for recording exposures with high energy radiation e.g. direct exposures with penetrating radiation or exposures with short duration high intensity visible light (flash exposures of 10^{-3} sec or less) because with these exposures wherein the latent image forms under similar conditions namely the passage of an electron through a silver halide grain in a very short time, a smaller proportion of the radiant energy is active for latent image formation at the surface of the grains than when the exposure occurs with light of low or moderate intensity (cfr. Mees and James, The theory of the photographic process, 3rd Ed., 1966, pages 126, 136 and 191).

25 In order to increase the overall sensitivity and more especially the surface sensitivity, emulsions can be chemically sensitized by means of sulphur sensitizers, reduction sensitizers and/or noble metal especially gold sensitizers, so as to create sensitivity specks especially at the surface of the grains whereby upon exposure of the grains latent image specks are formed at or in the immediate neighbourhood of these surface sensitivity specks.

30 According to Mees & James, The theory of the photographic process, 3rd Ed, 1966, page 125 sulphur sensitization generally not only increases surface sensitivity but also lowers internal sensitivity whereas reduction and gold sensitization often increase both internal and surface sensitivity. Radiographic materials for medical as well as industrial use are most commonly sensitized chemically by means of sulphur sensitization, together with gold sensitization.

35 The extent to which the surface sensitivity of emulsions can be increased by chemical sensitization is restricted because the chemical sensitization reaches a limit beyond which further addition of sensitizer or further digestion of the emulsion with the sensitizer merely

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increases the fog of the emulsion with constant or decreasing speed.

Direct exposure to penetrating radiation, contrary to exposure with the use of fluorescent intensifying screens which are commonly employed in medical radiography to convert X-ray exposures into visible light exposures and thus to reduce patient X-ray dosage substantially, have not only the disadvantage of forming predominantly internal latent image specks but also that only a small fraction of the incident radiation is absorbed by the emulsion. Therefore, commercial radiographic film materials for direct exposure to penetrating radiation which include e.g. industrial radiographic materials for non-destructive testing and medical radiographic materials for detecting breast diseases (mammography) have high coating weights of silver halide per unit area of film base, such coating weights corresponding to from 13 g to 40 g of silver nitrate per sq. m. (These amounts are up to six times the silver halide coating weights used in common negative emulsions for visible light recording and more than twice the coating weights of silver halide generally used in medical radiographic material for use with fluorescent screens).

Because the use of a very thick emulsion layer is inconvenient for development and fixation it is common practice to coat emulsion layers of radiographic materials on both sides of a transparent film support. Moreover, it is generally desirable for the required processing time of exposed photographic materials to be as short as possible. Techniques for rapid processing of exposed photographic elements are known. Usually, rapid processing occurs in automatic processing machines where the materials are conducted from one processing station to another by means of roller pairs or other transporting means. In order to accelerate processing of radiographic materials, it is not only desirable for a silver halide layer to be provided on each side of the support but also to limit the content of hydrophilic colloid binder in the emulsion layers so that effective penetration of processing liquids is accelerated. The weight ratio of hydrophilic colloid, more particularly gelatin, to silver halide, expressed as silver nitrate, is generally at most about 1:1.

Known radiographic silver halide materials of the type described hereinbefore which have high coating weights of silver halide and which in order to allow rapid processing have a low hydrophilic binder to halide ratio, show inferior image quality upon exposure and rapid-processing in automatic processing machines. The severe physical conditions to which the elements are subjected in the apparatus e.g. pressure and usually elevated temperature results in the formation of repeated pressure marks in the image, e.g. from roller pairs and other guiding means. These marks are highly undesirable in radiographic images as they may affect interpretation thereof.

In order to reduce the tendency to formation of pressure marks in silver halide emulsions, it has been described in the art to add to the photographic silver halide emulsions various synthetic polymeric materials e.g. poly-N-vinyl-lactams, acrylic polymers, more particularly polyacrylates having a glass transition temperature of less than 20°C (French Patent 1,571,047 filed August 24, 1968 by Kodak Ltd.), polymers of N-hydroxyalkyl(meth)acrylamides or ethers thereof (Belgian Patent 790,872 filed November 3, 1972 by Agfa-Gevaert N.V.), etc.

These synthetic polymeric materials reduce the tendency to the formation of pressure marks but form a supplemental ballast for the emulsion and may affect the photographic properties. Moreover, they were not found to be very effective in the high-sensitive radiographic elements for direct exposure as above specified.

According to the present invention, there is provided a radiographic material for direct exposure to penetrating radiation comprising a transparent support and on one or each side thereof a layer of a hydrophilic colloid silver halide emulsion, wherein:

(1) the total amount of silver halide per sq. m of said support corresponds to from 13 g to 40 g of silver nitrate;

(2) the halide of the silver halide emulsion is bromide or bromide together with chloride up to a maximum of 10 mole %, and/or iodide up to a maximum of 3 mole %, (the mole % being based on the total weight of halide).

(3) the ratio of hydrophilic colloid to silver halide, expressed as silver nitrate, is at most 1.0,

(4) the silver halide grains have an average grain diameter of at least 250 nm and are for at least 80% by weight regular in shape and

(5) the emulsion is such that, disregarding the effect of any chemical sensitization thereof, it has a surface sensitivity (measured at density 0.50 above fog according to normal photographic techniques by coating a test portion of a corresponding emulsion in non-chemically sensitized condition, on a conventional support at a coverage of silver halide corresponding to 10 g of silver nitrate per sq. m at a pH of 6.00 and a pAg of 8.00, exposing for 10^{-4} sec in a Mark VI Sensitometer of EG & G, Inc., Boston, Mass. USA described in EG & G's Data Sheet S7003B-1, printed June 1975, using a General Electric type FT 118 electronic flash tube with a radiant energy of 100 Wattsec and developing for 10

min at 20°C in the surface developer described hereinafter) at least equal to its internal sensitivity measured at density 0.50 above fog by coating and exposing an identical test portion in the same way as the first test portion, then bleaching the portion for 5 min at 20°C in an aqueous bleaching solution containing 30 g of potassium hexacyanoferrate (III) and 30 mg of phenosafranine per litre, and developing it for 15 min at 20°C in the internal developer set forth hereinafter:

Surface developer

10	p-monomethylaminophenol sulphate	2.50 g	10
	ascorbic acid	10.0 g	
	potassium bromide	1.0 g	
15	sodium metaborate-4-water	35.0 g	15
	water to make	1.0 l	

Internal developer

Same composition as surface developer to which 10 g of anhydrous sodium thiosulphate was added per litre.

In comparison with known radiographic materials, the materials according to the invention have a favourable combination of properties. They have good resistance to the formation of pressure marks in rapid processing apparatus and they have improved sensitivity for direct exposure to penetrating radiation as compared with conventional radiographic emulsions for such exposures.

The halide of the silver halide emulsion may comprise, in addition to silver bromide, silver bromochloride, silver bromoiodide and/or silver bromochloroiodide grains provided that the amounts of chloride and iodide do not exceed the limits above specified.

The emulsion layer(s) has (have) a high primitive surface sensitivity for direct exposure to penetrating radiation. In other words, before any chemical sensitization of the silver halide grains their surface sensitivity for high-intensity exposures is at least equal to and preferably surpasses their internal sensitivity for such exposures.

The distribution of the primitive surface sensitivity for high intensity exposures i.e. the sensitivity for high intensity exposures before any chemical sensitizers others than those that could be present in an inert photographic gelatin have been added, can easily be determined as is known in the art by comparing the sensitivity obtained after high intensity exposure and development of the surface latent image in a surface developer with the sensitivity obtained after high intensity exposure, bleaching of the surface latent image and development of the internal latent image in an internal developer.

The total amount of silver halide per sq. m is preferably from 18 g to 30 g of silver nitrate. Emulsions of the type described having a primitive surface sensitivity for high intensity exposures equal to or higher than the primitive internal sensitivity and having substantially regular shape can be prepared by controlling the reaction conditions during the steps of grain-formation and grain growth.

Precipitation of the silver halide grains is most advantageously, effected by the double-jet technique wherein an aqueous solution of silver nitrate and an aqueous solution of the halide(s) are simultaneously run into an agitated aqueous solution of a peptizer, e.g. gelatin or a gelatin derivative. To avoid as much as possible the formation of internal sensitivity specks for high intensity exposures the peptizer is photographically inert and precipitation of the silver halide grains is effected in the substantial absence of any sensitizing compounds or metal compounds producing centres promoting the deposition of photolytic silver. To obtain the desired average grain-size, which according to the present invention is at least 250 nm and is preferably between 250 nm and 1200 nm the precipitation is most advantageously effected in the presence of a silver halide solvent e.g. ammonia, a water-soluble thiocyanate such as potassium or ammonium thiocyanate, or a thioether silver halide solvent e.g. of the type described in US Patent 3,574,628 of Evan T. Jones issued April 13, 1971 and in published German Patent Application 2,614,862 filed April 6, 1976 by Agfa-Gevaert A. G. The silver halide solvent can be added to the precipitation medium before addition of the silver salt and halide solutions and/or it may be added with the silver salt and halide solution at any time during addition of the latter e.g. via one of the

jets of these solutions or via a separate jet.

During silver halide grain-formation the temperature is generally between 30°C and 90°C, and it is preferably at least 50°C. In the absence of ammonia as silver halide solvent, the pH is generally maintained at a value between 2 and 9. The pAg is preferably not too high when a silver halide solvent is used in order to avoid competition between the silver halide solvent and the excess halide ions which may also act as silver halide solvent. The pAg is generally between 6 and 11, preferably between 7.5 and 10.0

Silver halide emulsions with grains of substantially regular shape are known. As disclosed in a paper entitled "Fundamental Aspects of Growth and Shape of Photographic Silver Halide Crystals", published in The Proceedings of the 5th International Conference on Nuclear Photography held at Cern, Geneva, Sept. 15-18, 1965, edited by E. Dahl-Jensen, regular silver halide grains or crystals are obtained by isotropic growth occurring simultaneously and uniformly on all crystal faces. Such crystals develop (1, 0, 0) or (1, 1, 1) faces and are free of twin plane stacking faults, e.g., twin planes such as (1, 1, 1) twin planes. A (1, 1, 1) twin plane is a stacking fault which arises when a silver halide crystal grows in such a manner as to alter the previously established order of stacking of (1, 1, 1) planes in forming the crystal.

Photographic silver halide emulsions comprising silver halide grains of regular shape or structure can be obtained by controlling the reaction conditions during the double-run grain-formation procedure. Depending upon these conditions the regular silver halide grains will be characterized by a certain crystal habit, e.g., cubic, cubo-octahedral and/or octahedral, and will exhibit certain planes, e.g., (1, 0, 0) or (1, 1, 1) planes, as crystal faces. For example, in an article entitled, "Precipitation of Twinned AgBr Crystals", by Berry and Skillman, Photographic Science and Engineering, vol. 6, No. 3, May-June 1962, it is known that by a change in pAg it is possible to conduct a double-run precipitation of silver halide in such a manner that regular cubes or octahedra are formed. To obtain substantially regular grains a large excess of halide ion is generally avoided. The conditions employed during the preparation of the silver halide grains are inter-related and a change in one variable such as pAg, pH, etc., while maintaining other conditions constant can change the silver halide crystal structure. In addition to previous references, a suitable method for preparing photographic silver halide emulsions having the required regular shape is also disclosed in the article entitled, "1a: Properties of Photographic Emulsion Grains", by Klein and Moisar, The Journal of Photographic Science, vol 12, 1964, pp. 242-251. A preferred class of photographic silver halide emulsions employed in the practice of this invention contains regular cubic or cubo-octahedral grains.

The silver halide emulsions of materials according to the present invention, which emulsions incorporate silver halide grains of substantially regular shape and have a primitive surface sensitivity at least equal to the primitive internal sensitivity can be further characterized as having a low level of grain disorder. Methods for assessing grain-disorder have been described in an article entitled: "Grain Disorder and Its Influence on Emulsion Response" by G. C. Farnell et al, The Journal of Photographic Science, Vol 24, 1976, pp. 1-11.

As is apparent from the Klein-Moisar article referred to hereinbefore silver halide emulsions having grains of substantially regular shape include monodisperse emulsions having grains of substantially uniform grain-size. Mono-dispersed emulsions are emulsions wherein at least about 80% and generally at least 90-95% by weight of the grains have a diameter which is within about 40%, more particularly within about 30% of the mean grain-diameter. Mean grain-diameter can be determined by 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 Jones "The theory of the photographic process" (1966), Chapter II.

The silver halide emulsions used according to the present invention to form radiographic materials for direct-exposure to penetrating radiation need not be monodisperse emulsions of substantially uniform grain-size. They may for example be composed of mixtures of monodisperse emulsions having grains of different mean grain diameter the mixtures thus being actually heterodisperse emulsions.

As referred to hereinbefore precipitation may occur in the presence of a silver halide solvent e.g. ammonia, a water-soluble thiocyanate such as potassium or ammonium thiocyanate, or a thioether silver halide solvent e.g. a thioether compound of the type described in US Patent 3,574,628, already mentioned hereinbefore, e.g. 1,8-dihydroxy-3,6-dithiaoctane, 1,10-dithia-4,7,13,16-tetraoxacyclooctadecane, 3,15-dioxa-6,9,12-trithioheptadecane, 1,7-dithia-4,10-dioxacyclododecane, 1,17-di(N-ethylcarbamy)-6,12-dithia-9-oxaheptadecane, or 6,9-dioxa-3,12-dithiatetra-decane, and methionine, ethionine and structurally related thioether compounds having besides thioether S-atom(s) amino and/or carboxyl groups in acid or salt form e.g. S-alkyl cysteines,

including derivatives of these thioether compounds e.g. esters and amides, as described in published German Patent Application 2,614,862, mentioned hereinbefore. The silver halide solvent may be added to the precipitation medium before addition of the silver salt and halide solutions and/or it may be added with the silver salt and halide solution at any time during addition of the latter e.g. via one of the jets of these solutions or via a separate jet.

In the preparation of the emulsions for use according to the present invention, washing of the emulsions after grain-formation and grain-growth, can be effected by any suitable technique e.g. by leaching in cold water the chill-set and shredded emulsion or by coagulation techniques using e.g. an acid-coagulable gelatin derivative such as phthaloyl gelatin and N-phenylcarbamoyl gelatin (as described in US Patent Specifications 2,614,928 of Henry C. Yutze and Gordon F. Frame, 2,614,929 of Henry C. Yutze and Frederick J. Russell, both issued October 21, 1952, and 2,728,662 of Henry C. Yutze and Gordon F. Frame, issued December 27, 1955) or anionic polymers e.g. polystyrene sulphonic acid and sulphonated copolymers of styrene (e.g. as described in German Patent 1,085,422 filed October 16, 1958 by Agfa A.G.).

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 about 35 to about 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. Instead or in addition to normal gelatin, which is preferably used, other known photographic hydrophilic colloids can also be used for redispersion and for forming the binder of the silver halide emulsion e.g. a gelatin derivative as referred to above, other natural hydrophilic colloids e.g. albumin, zein, agar-agar, gum arabic, alginic acid, and derivatives thereof e.g. salts, amides and esters, starch and derivatives thereof, cellulose derivatives e.g. cellulose ethers, partially hydrolyzed cellulose acetate, carboxymethyl cellulose, etc. or synthetic hydrophilic resins, e.g. polyvinyl alcohol, polyvinyl pyrrolidone, homo- and copolymers of acrylic and methacrylic acid or derivatives e.g. esters, amides and nitriles, vinyl polymers e.g. vinyl ethers and vinyl esters.

The amount of hydrophilic colloid in the redispersed emulsion is such that the ultimate emulsion has a ratio by weight of hydrophilic colloid to silver halide, expressed as silver nitrate, which is at most 1.0. It is generally comprised between 0.2 and 0.8 and most preferably between 0.3 and 0.6.

The silver halide emulsions of materials according to the present invention having a high primitive surface sensitivity may be further chemically sensitized by any of the accepted procedures, including sulphur sensitization, reduction sensitization and/or noble-metal sensitization e.g. as described on page 107 of the December 1971 issue of "Product Licensing Index" published by Industrial Opportunities Ltd., Havant, England and in the patent literature referred to therein. The emulsion may be digested in the presence of small amounts of sulphur group sensitizers e.g. sulphur, selenium and tellurium sensitizers, e.g. allyl isothiocyanate, thiourea, allyl thiourea, sodium thiosulphate, thioacetamide, allyl selenourea, allyl tellurourea, colloidal selenium, etc. The emulsion may also be sensitized by means of reductors e.g. tin compounds as described in Belgian Patents 493,464 filed January 24, 1950 and 568,687 filed June 18, 1958 both by Gevaert Photo-Producten N.V., iminoamino-methane sulphinic acids as described in British Patent 789,823 filed April 24, 1955 by Gevaert Photo-Producten N.V., polyamines e.g. diethylene triamine, spermine and bis(β -amino-ethyl)sulphide, thiourea dioxide, etc. Reduction sensitization may also occur by digestion at low pAg values as described by H. W. Wood, J. Phot. Sci. 1 (1953) 163 or by hydrogen-sensitization as described in USP 3,891,446 of Gaile A. Janusonis issued June 24, 1975, the published German Patent Application DT OS 2,144,994 filed September 8, 1971 by Kodak Ltd. and J. Phot. Sci. Vol. 24, No. 1 page 19.

The emulsions may also be sensitized by noble metal sensitization. Noble metal sensitization preferably occurs by digestion with a gold compound but any of the other known noble metal sensitizers e.g. ruthenium, rhodium, palladium, iridium and platinum compounds as described by R. Koslowsky, Z. Wiss. Phot. 46, 65-72 (1951) may be used. Representative examples of noble metal sensitizers are gold(III) chloride, gold(I) sulphide, potassium aurithiocyanate, potassium chloroaurate, ammonium chloropalladate, potassium chloroplatinate, etc.

For the preparation of the radiographic material according to the present invention the silver halide emulsions are preferably chemically sensitized by reduction sensitization combined with noble metal sensitization more particularly gold sensitization which leads to favourable relationship between average grain-size, sensitivity and fog.

The emulsions may comprise compounds that sensitize the emulsion by development acceleration for example alkylene oxide polymers. These alkylene oxide polymers may be

of various type e.g. polyethylene glycol having a molecular weight of 1500 or more, alkylene oxide condensation products or polymers as described among others in United States Patent Specifications 1,970,578 of Conrad Schoeller and Max Wittner issued August 21, 1934, 2,240,472 of Donald R. Swan issued April 29, 1941, 2,423,549 of Ralph Kinsley Blake, William Alexander Stanton and Ferdinand Schulze issued July 8, 1947, 2,441,389 of Ralph Kinsley Blake issued May 11, 1948, 2,531,832 of William Alexander Stanton issued November 28, 1950, and 2,533,990 of Ralph Kinsley Blake issued December 12, 1950, in United Kingdom Patent Specifications 920,637 filed May 7, 1959, 940,051 filed November 1, 1961, 945,340 filed October 23, 1961 all by Gevaert Photo-Producten N.V. and 991,608 filed June 14, 1961 by Kodak Co., in Belgian Patent Specification 648,710 filed June 2, 1964 by Gevaert-Photo-Producten N.V., and in the published German Patent Applications DT-OS 2,426,177 filed May 28, 1974 and 2,601,779 filed January 20, 1976 by Agfa-Gevaert A.G. Other compounds that sensitize the emulsion by development acceleration and that are suitable for use in the emulsion according to the invention have been described in US Patents 3,523,796 and 3,523,797 of Jozef Frans Willems, Francis Jeanne Sels and Robrecht Julius Thiers both issued August 11, 1970, 3,552,968 of Jozef Frans Willems, issued January 5, 1971, 3,746,545 of Robert Joseph Pollet, Jozef Frans Willems, Francis Jeanne Sels and Herman Adelbert Philippaerts, issued July 17, 1973 and 3,749,574 of Robert Joseph Pollet, Francis Jeanne Sels and Herman Adelbert Philippaerts, issued July 31, 1973.

Other development accelerating compounds are onium and polyonium compounds preferably of the ammonium, phosphonium, and sulphonium type for example trialkyl sulphonium salts such as dimethyl-n-nonyl sulphonium p-toluene sulphonate, tetra-alkyl ammonium salts such as dodecyl trimethyl ammonium p-toluene sulphonate, alkyl pyridinium and alkyl quinolinium salts such as 1-m-nitrobenzyl quinolinium chloride and 1-dodecyl pyridinium chloride, bis-alkylene pyridinium salts such as N,N-tetramethylene bispyridinium chloride, quaternary ammonium, sulphonium phosphonium polyoxyalkylene salts, especially polyoxyalkylene bispyridinium salts. Examples of suitable onium compounds can be found in United States Patents 2,275,727 and 2,288,226 both of Burt H. Carroll and Charles F. H. Allen issued March 10, 1942 and June 30, 1942 respectively, 2,944,900 of Burt H. Carroll, Hubert S. Elins, James L. Graham and Charles V. Wilson and 2,944,902 of Burt H. Carroll, John Sagal Jr. and Dorothy J. Beavers, both issued July 12, 1960, French Patent 1,506,229 filed December 28, 1966 by Agfa A.G. and the published German Patent Application DT-OS 2,508,280 filed February 26, 1975 by Agfa-Gevaert A. G. Also suitable are organic compounds comprising thioether S-atoms e.g. of the type described in US Patents 3,046,129 of James L. Graham and John Sagal Jr., 3,046,132 and 3,046,133 both of Louis M. Minsk, 3,046,134 of John R. Dann and Jonas J. Chechak, all issued June 24, 1962 and 3,036,134 of William Judson Mattox issued May 22, 1962, in French Patent 1,351,410 filed September 6, 1962 by Kodak Co., in British Patents 931,018 filed April 7, 1961 by Agfa A.G. and 1,249,248 filed December 9, 1969 by Konishiroku Photo Industry Co. Ltd., and in the published German Patent applications 2,360,878 filed December 6, 1973, 2,601,779 and 2,601,814 both filed January 20, 1976, all by Agfa-Gevaert A.G.

The emulsions may comprise the common emulsion stabilizers e.g. homopolar or salt-like compounds of mercury with aromatic and heterocyclic rings (e.g. mercaptotriazoles) simple mercury compounds, mercury sulphonium double salts and other mercury compounds of the kind described in Belgian Patent Specifications 524,121 filed November 7, 1953 by Kodak Co., 677,337 filed March 4, 1966, 707,386 filed December 1, 1967 and 709,195 filed January 11, 1968 all by Gevaert-Agfa N.V. Other suitable and preferred emulsion stabilizers are the well-known azaindenes, particularly the tetra- or pentaazaindenes and especially those substituted by hydroxy- or amino groups. Suchlike compounds have been described by Birr in Z. Wiss. Phot. 47, 2-58 (1952) and in US Patents 2,444,605 of Newton Heimbach and Walter Kelly, Jr., 2,444,607 of Newton Heimbach, 2,44,609 of Newton Heimbach and Robert H. Clark, all issued July 6, 1948 and 2,450,397 of Newton Heimbach, issued September 28, 1948. The emulsions may further comprise as stabilizers heterocyclic nitrogen-containing mercapto compounds such as benzothiazoline-2-thione and 1-phenyl-5-mercaptopotetrazole, sulphinic acids and seleninic acids as described in US Patent 2,057,764 of Johannes Brunken, issued October 20, 1936, representatives of which are benzenesulphinic acid and toluenesulphinic acid, in acid or salt form, the amide stabilizers e.g. acetamide described in British Patent 1,325,878 filed November 3, 1969 by Gevaert-Agfa N.V. and the disulphides described in US Patent 3,761,277 of Antoon Leon Vandenberghe, Jozef Frans Willems, Robert Joseph Pollet, Gaston Jacob Benoy and Marcel Karel Van Doorselaer. Especially suitable are thiosulphonic acids in acid or salt form as described in US Patent 2,394,198 of Fritz W. H. Mueller, issued February 5, 1946, representatives of which are benzenethiosulphonic acid, toluenethiosulphonic sodium salt, p-chloro-benzenethiosulphonic acid sodium salt, propylthiosulphonic acid potassium salt,

butylthiosulphonic acid potassium salt, as well as derivatives of these thiosulphonic acids e.g. the polythionic acids and thioanhydrides of sulphonic acids described in US Patent 2,440,206 of Fritz W. H. Mueller, issued April 20, 1948, e.g. dibenzene disulphonyl trisulphide. Other very suitable emulsion stabilizers are the selenium compounds of the type described in GBP 1,323,111 filed April 1, 1970 by Agfa-Gevaert N.V. which include diselenides and selenocyanates e.g. di(3-carboxypropyl) diselenide, di(2-aminoethyl) diselenide hydrochloride, di(2-acetylaminoethyl)diselenide, di(2-benzoylaminoethyl)diselenide, dibenzyl diselenide, diphenyl diselenide, di- β -naphthyl diselenide, di(p-bromophenyl)diselenide, di(p-chlorophenyl)diselenide, di(m-chlorophenyl)diselenide, di(m-carboxyphenyl)diselenide, di(p-carboxyphenyl)diselenide, di(p-nitrophenyl)diselenide, di(3-indolyl)diselenide, hexadecylselenocyanate, 2-carboxyethylselenocyanate, 3-sulphopropyl-selenocyanate, carbamoylmethylselenocyanate, phenylselenocyanate, p-chlorophenylselenocyanate, m-chlorophenylselenocyanate, p-bromophenylselenocyanate and p-nitrophenylselenocyanate, and 2-methyl-benzthiazoyl-6-selenocyanate. The above sulphonic acids, seleninic acids, thiosulphonic acids and derivatives and selenium compounds are preferably used at the stage of chemical sensitization or added to the emulsion immediately thereafter. The emulsions according to the present invention are preferably stabilized by means of azaindene stabilizers as referred to above and a member selected from carbocyclic aromatic thiosulphonic acids or salts thereof, carbocyclic aromatic diselenides and carbocyclic aromatic selenocyanates representative examples of which have been given hereinbefore.

The materials of the invention may further comprise or be developed in the presence of compounds that are particularly effective as antifoggants for materials that are processed at elevated temperatures e.g. heterocyclic compounds with nitro-substituents e.g. nitroindazole and nitrobenzotriazole as described in French Patent Specification 2,008,245 filed May 9, 1969 by Eastman Kodak Co, 1H-6-methylbenzotriazole, nitrobenzylidene pyridinium and nitrobenzylidene quinolinium compounds as well as the onium compounds described in published German Patent Application 2,040,876 filed August 18, 1970 by Konishiroku Photo Industry Co. Ltd.; further the nitrobenzene compounds described in British Patent 1,399,449 filed September 17, 1971 by Agfa-Gevaert N.V. and the nitrile compounds described in British Patent 1,395,161 filed September 17, 1971 by Agfa-Gevaert N.V. The developer may also comprise development accelerators e.g. polyoxyalkylene compounds and onium compounds of the type referred to hereinbefore.

When materials according to the invention and incorporating reduction-sensitized emulsions, are developed in developers comprising a high concentration of silver halide solvent e.g. sulphite ion, the developers preferably also comprise antifoggants as disclosed in RD 13654 of the August 1975 issue of "Research Disclosure" Havant, England, e.g. azaindenes and heterocyclic mercapto compounds as referred to hereinbefore for use in the emulsion.

The photographic silver halide materials may further comprise surface-active compounds, which include anionic, non-ionic and amphoteric surfactants, e.g. long-chain aliphatic sulphates, sulphonates and carboxylates or alkylaryl sulphates, sulphonates and carboxylates which may comprise recurring ethylene oxide units, polyoxyethylene compounds, the fluorinated surfactants of Belgian Patent Specification 742,680 filed December 5, 1969 by Gevaert-Agfa N.V., etc. plasticizers, matting agents, e.g. polymethyl methacrylate and silica particles, compounds increasing silver covering power e.g. dextran, lactose, poly-N-vinylactams, etc., colour couplers, hardening agents e.g. formaldehyde, dialdehydes, halogen-substituted aldehyde acids such as mucochloric and mucobromic acid, hardening accelerators e.g. recorsinol, phloroglucinol, etc.

A wide variety of transparent supports known for use in photographic silver halide elements can be used for the emulsion layer(s). Such supports include cellulose nitrate film, cellulose acetate film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films of resinous materials.

The materials of the present invention incorporate silver halide in a total amount corresponding to from 13 g to 40 g of silver nitrate per sq. m of support. For recording X-ray exposures or exposures with other penetrating radiation, the emulsion is generally coated on both sides of the support, the coating weight for each side corresponding to from 6.5 g to 20 g of silver nitrate per sq. m of support.

In the automatic processing, especially at elevated temperatures, of radiographic materials according to the present invention it is preferred to use a hardening developer. In such developers the hardening agent is generally an aldehyde hardener, particularly aliphatic dialdehydes e.g. maleic aldehyde and glutaraldehyde, which may be used as such or in the form of their bisulphite addition products.

The following examples illustrate the present invention.

EXAMPLE 1

Emulsion I (comparison emulsion)

A conventional ammoniacal heterodisperse and irregular silver bromiodide emulsion for non-destructive testing with an average grain diameter of 700 nm and containing 0.35 mole % of iodide was prepared by adding over a period of about 7 minutes a 3 molar ammoniacal silver nitrate solution to an agitated aqueous gelatin solution to which a 3 molar ammonium bromide and 3 molar potassium iodide solution had been added in an amount equivalent to the amount of silver nitrate and so that the above ratio of bromide to iodide is obtained. The temperature was kept at 38°C.

After a physical ripening stage of 4 minutes, the emulsion was coagulated by the addition of ammonium sulphate, washed and redispersed in the usual manner.

Finally, water and gelatin were added in order to obtain a concentration of silver halide expressed as silver nitrate, of 200 g per kg emulsion and a ratio of gelatin to silver halide (expressed as silver nitrate) of 0.4.

Emulsion II

A monodispersed cubo-octahedral regular silver bromide emulsion, having an average grain size of 800 nm was prepared by adding simultaneously over a period of about 45 minutes a 3 molar aqueous solution of silver nitrate and a 3 molar aqueous solution of potassium bromide at a rate of 50 ml/minute to an agitated gelatin solution containing 40 g of dl-methionine.

The temperature was maintained at 65°C, the pH at 4 and the pAg at 8.2 during the precipitation. After a physical ripening stage of 10 minutes, the emulsion was cooled to 40°C and the pH was lowered to 3 by the addition of diluted sulphuric acid. The emulsion was coagulated by adding a solution of polystyrene sulphonic acid, washed and redispersed in the usual manner.

Finally, water and gelatin were added in order to obtain a concentration of silver halide expressed as silver nitrate of 200 g per kg emulsion and a ratio of gelatin to silver halide (expressed as silver nitrate) of 0.4.

Emulsion III

A monodispersed cubo-octahedral regular silver bromiodide emulsion having an average grain diameter of 700 nm and containing approximately 0.5 mole % of iodide is prepared by adding simultaneously an ammoniacal silver nitrate solution and an aqueous solution of potassium bromide and potassium iodide (the halide being used in an excess amount of 15 mole %) to an agitated aqueous gelatin solution brought at a pH of 3 by the addition of dilute sulphuric acid. The temperature throughout the addition is maintained at 50°C.

The emulsion was thereafter coagulated with polystyrene sulphonic acid, the coagulation being effected at a pH of 3.5. The resulting coagulant was washed and redispersed in the usual manner. Water and gelatin were added in order to obtain a concentration of 200 g of silver halide, expressed as silver nitrate, per kg of emulsion and a ratio of gelatin to silver halide, expressed as silver nitrate, of 0.4.

In order to determine the internal and surface sensitivity for high energy exposures of the primitive emulsions made, test portions of the emulsions were coated at pH 6.0 and pAg 8.0 on one side of a film support at coverages of 10 g of silver halide, expressed as silver nitrate, per sq. m. and the coated emulsions were exposed for 10^{-4} sec in a Mark VI Sensitometer of EG&G, Inc., Boston, Mass., USA using a General Electric type FT 118 electronic flash tube with a radiant energy of 100 Wattsec.

The surface sensitivity was measured at density 0.5 above fog after processing as follows:
5 min rinsing in running tap water (15°C)
10 min development at 20°C in the surface developer of the composition:

55	p-monomethylaminophenol sulphate	2.50 g	55
	d-isoascorbic acid	10.0 g	
	potassium bromide	1.0 g	
60	sodium metaborate-4-water	35.0 g	60
	water to make	1.0 litre	

5 min rinsing in running tap water (15°C)
10 min fixing at 20°C in the fixing bath of the following composition:

5	anhydrous sodium thiosulphate	130.0 g	5
	potassium metabisulphite	25.0 g	
	water to make	1.0 litre (pH: 4.55)	

10 and

15 10 min rinsing in running tap water (15°C)
The internal sensitivity was measured at density 0.5 above fog after processing as follows:
15 5 min rinsing in running tap water (15°C)
5 min treating at 20°C in an aqueous bleaching solution containing 30 g of
potassium hexacyanoferrate (III) and 30 mg of phenosafranine per litre,
5 min rinsing in running tap water (15°C)
20 15 min development at 20°C in the internal developer of the composition obtained
by adding 10 g of anhydrous sodium thiosulphate to 1 litre of the above surface
20 developer,
5 min rinsing in running tap water (15°C)
10 min fixing at 20°C in the above fixing solution, and
25 10 min rinsing in running tap water.

25 The results are listed in the following table 1. The values given for the relative sensitivity
are log Et values. The sensitivity is higher as the log Et values are lower with $\Delta \log Et$ equal
to 0.30 meaning a sensitivity increase or decrease by a factor 2.

30 TABLE 1

30	emulsion	relative surface sensitivity (log Et values)	relative internal sensitivity (log Et values)	30
35	I	1.72	1.35	35
	II	1.25	1.93	
40	III	1.20	>3.00	40

40 From the above values it is apparent that emulsions II and III have higher primitive
surface sensitivity than emulsion I and that contrary to emulsion I their primitive surface
sensitivity outranges their primitive internal sensitivity. Taking into account that $\Delta \log Et =$
45 0.30 means a factor 2 it can be calculated that the ratio of relative internal sensitivity to
relative surface sensitivity is for emulsion I 100:57 for emulsion II 100:478 and for emulsion
45 III 100:6400.

50 The emulsions, I, II and III were divided into several aliquot portions. Of each emulsion
type, some portions were chemically sensitized using the sensitizers listed in the table
hereinafter while other portions were not chemically sensitized. Moreover, some portions
50 were stabilized by addition of a stabilizer while others were not. After addition of hardener,
resorcinol and coating aid, the emulsion portions were coated on both sides of a film
support so that per side about 13 g of silver halide (expressed as silver nitrate) was present
per sq. m.

55 The photographic elements formed were exposed in a sensitometer and then processed in
a 90 seconds automatic processing machine wherein the elements were developed for 20
seconds at 38°C in a developer comprising hydroquinone and N-monomethyl-p-
aminophenol as developing agents and glutar-aldehyde as hardener.

60 After processing the elements were evaluated visually as regards the pressure marks
formed. The elements are given a value from 0 to 5 where 0 stands for no pressure marks
and 5 stands for heavy formation of pressure marks. The values given are listed in the
following table.

	chemical sensitizers (mg/mole AgBr)	5-methyl-7-hydroxy- s-triazolo[1,5-a]- pyrimidine as sta- bilizer (mg/mole AgBr)	value for pressure marks in the elements with			
			emul- sion I (com- pari- son)	emul- sion II	emul- sion III	
5						5
10	none	none	1	0	0	10
	none	222 mg	1	0	0	
15	1.02 mg of anhydrous sodium thiosulphate	222 mg	2	0	0	15
20	0.068 mg of thio- urea dioxide + 0.306 mg of hydro- gen tetrachloro- aurate (III)	none	2	0	0	20
25	do	222 mg	4	2	1	25
30	0.136 mg of thio- urea dioxide + 0.612 mg of hydro- gen tetrachloro- aurate (III) + 0.68 mg of toluene thiosulphonic acid	none	5	0	1	30

35 The above results show that as compared with the ammoniacal heterodisperse, irregular emulsion, the emulsions according to the present invention show less tendency to formation of pressure marks. 35

EXAMPLE 2

40 The emulsions I, II and III were reduction and gold-sensitized in the presence of toluene thiosulphonic acid by addition of 1.4 mg of thiourea dioxide, 1.05 mg of hydrogen tetrachloro aurate(I)-4-water and 0.7 mg of toluene thiosulphonic acid per mole of silver halide and heating at 50°C, pAg 8.2 and pH 6.5 until the optimum sensitivity-fog relationship was reached (3 h 30 min). 40

45 To each of the chemically sensitized emulsions, 5-methyl-7-hydroxy-s-triazolo-[1,5-a]pyrimidine was added as an emulsion stabilizer in an amount of 5 mmole per mole of silver halide. After addition of coating aids the emulsions were coated at pH 5 and pAg 8.5 on both sides of a film support at a total coverage of silver halide corresponding to 30 g per sq. m of silver nitrate. 45

50 The materials obtained were exposed in an X-ray sensitometer using a röntgen tube so that at a distance of one yard the half layer value is 0.5 mm Cu (about 83 kV and 10 mA). 50

The exposed emulsions were developed for 7 min at 21°C in a developer comprising:

	p-monomethylaminophenol sulphate	3.5 g	
	anhydrous sodium sulphite	60 g	
5	hydroquinone	10 g	5
	boric acid	7.5 g	
10	sodium hydroxide	17.5 g	10
	potassium bromide	4 g	
15	water to make	1000 ml (pH \pm 11)	15

and then fixed and rinsed in the usual way.

The sensitometric values obtained with fresh materials and materials stored before exposure and processing for 36 hours at 57°C and 34% relative humidity are listed in the following table 1. The values given for the speed are relative log Et values measured at density 2 above fog. A decrease of the value by 0.30 means a doubling of the speed.

TABLE 1

25	emulsion	fresh materials			stored materials			25
		fog	relative speed	gamma	fog	relative speed	gamma	
	I	0.15	1.43	4.22	0.24	1.42	4.84	
30	II	0.05	1.25	4.61	0.05	1.24	4.41	30
	III	0.04	1.25	4.76	0.03	1.19	4.84	

From the above results it is apparent that the materials containing emulsion layers from emulsions II and III according to the present invention have higher speed and better fog values than the material with the comparison emulsion I. The emulsions are also characterized by high stability against fog increase and speed decrease upon storing.

EXAMPLE 3

Emulsions I and II of example 1 were chemically sensitized by one of the following procedures:

- A. Reduction and gold sensitization in the presence of toluene thiosulphonic acid by addition of 1.4 mg of thiourea dioxide, 1.05 mg of hydrogen tetrachloroaurate(I)-4-water and 0.7 mg of toluene thiosulphonic acid per mole of silver halide and heating at 50°C, pH 6.5 and pAg 8.2 until the optimum sensitivity-fog relationship was reached.
- B. Sulphur and gold sensitization in the presence of toluene thiosulphonic acid by addition of 1.05 mg of sodium thiosulphate, 1.8 ml of a $1.5 \cdot 10^{-3}$ molar solution of potassium aurithiocyanate and 1.3 mg of sodium sulphite and 0.7 mg of toluenethiosulphonic acid per mole of silver halide and heating at 50°C pAg 7.8 and pH 6 until the optimum sensitivity-fog relationship was reached.

To each of the chemically sensitized emulsions 5-methyl-7-hydroxy-s-triazolo[1,5-a]pyrimidine was added in an amount of 5 mmole per mole of silver halide. After addition of coating aids the emulsions were coated at pH 5 and pAg 8.5 on both sides of a film support at a total coverage of silver halide corresponding to 30 g per sq. m of silver nitrate. The emulsion layers were overcoated with a gelatin antistress layer.

The materials obtained were exposed in an X-ray sensitometer and then processed as described in Example 2. The relative speed and fog values obtained with fresh materials and materials stored before exposure and processing for 36 hours at 57°C and 34% relative humidity are listed in the following table 2. The values given for the relative speed are relative Log Et values measured at density 2 above fog. A decrease of the value by 0.30 means a doubling of the speed.

TABLE 2

	emulsion	chemical sensitization	fresh material fog	rel. speed	stored material fog	rel. speed	
5	I	A	0.04	1.69	0.04	1.59	5
		B	0.15	1.31	0.21	1.31	
10	II	A	0.06	1.19	0.07	1.19	10
		B	0.18	1.16	0.27	1.14	
15	The above results show that emulsion II has higher speed than emulsion I for X-ray exposures.						15
	They also learn that whereas for emulsion II approximately the same speed values are obtained by the two chemical sensitization procedures, highest speed is obtained for conventional emulsion I by a combined sulphur-gold sensitization (B).						
20	WHAT WE CLAIM IS:						20
	1. A radiographic material for direct exposure to penetrating radiation comprising a transparent support and on one or each side thereof a layer of a hydrophilic colloid silver halide emulsion, wherein:						
25	(1) the total amount of silver halide per sq. m of said support corresponds to from 13 g to 40 g of silver nitrate,						25
	(2) the halide of the silver halide emulsion is bromide or bromide together with chloride up to a maximum of 10 mole %, and/or iodide up to a maximum of 3 mole %, (the mole % being based on the total weight of halide),						
30	(3) the ratio of hydrophilic colloid to silver halide, expressed as silver nitrate, is at most 1.0,						30
	(4) the silver halide grains have an average grain diameter of at least 250 nm and are for at least 80% by weight regular in shape and						
35	(5) the emulsion is such that disregarding the effect of any chemical sensitization thereof, it has a surface sensitivity (measured at density 0.50 above fog according to normal photographic techniques by coating a test portion of a corresponding emulsion, in non-chemically sensitized condition, on a conventional support at a coverage of silver halide corresponding to 10 g of silver nitrate per sq. m at a pH of 6.00 and a pAg of 8.00, exposing for 10^{-4} sec in a Mark VI Sensitometer of EG & G, Inc., Boston, Mass. USA described in EG & G's Data Sheet S70038-1, printed June 1975, using a General Electric type FT 118 electronic flash tube with a radiant energy of 100 Wattsec and developing for 10 min at 20°C in the surface developer described hereinafter) at least equal to its internal sensitivity measured at density 0.50 above fog by coating and exposing an identical test portion in the same way as the first test portion, then bleaching the portion for 5 min at 20°C in an aqueous bleaching solution containing 30 g of potassium hexacyanoferrate (III) and 30 mg of phenosafranine per litre, and developing it for 15 min at 20°C in the internal developer set hereinafter:						35
40							40
45							45
50	<i>Surface developer</i>						50
	p-monomethylaminophenol sulphate			2.50 g			
	ascorbic acid			10.0 g			
55	potassium bromide			1.0 g		55	
	sodium metaborate-4-water			35.0 g			
60	water to make			1.0 l		60	
	<i>Internal developer</i>						
	Same composition as surface developer to which 10g of anhydrous sodium thiosulphate was added per litre.						

2. A radiographic material according to claim 1, wherein in the silver halide emulsion at least 80% by weight of the silver halide grains have a diameter which is within 40% of the mean grain diameter.
- 5 3. A radiographic material according to claim 1 or 2, wherein in the silver halide emulsion the ratio of hydrophilic colloid to silver halide, expressed as silver nitrate, is between 0.2 and 0.8. 5
4. A radiographic material according to any of the preceding claims, wherein the silver halide emulsion has been chemically sensitized by reduction sensitization, sulphur sensitization and/or noble metal sensitization.
- 10 5. A radiographic material according to claim 4, wherein the emulsion has been chemically sensitized by a combined reduction-gold sensitization. 10
6. A radiographic material according to claim 5, wherein reduction sensitization occurred by digestion of the emulsion with thiourea dioxide.
- 15 7. A radiographic material according to claim 5, wherein reduction sensitization occurred by digestion at low pAg values. 15
8. A radiographic material according to any of the preceding claims wherein the emulsion comprises a stabilizing amount of a thiosulphonic acid, diselenide or selenocyanate.
- 20 9. A radiographic material according to claim 8, wherein the emulsion comprises a stabilizing amount of a carbocyclic aromatic thiosulphonic acid, a carbocyclic aromatic diselenide or a carbocyclic aromatic selenocyanate. 20
10. A radiographic material according to claim 8 or 9, wherein the thiosulphonic acid, diselenide or selenocyanate has been added at the stage of chemical sensitization of the emulsion.
- 25 11. A radiographic material according to any of the preceding claims wherein the emulsion also comprises an azaindene emulsion stabilizer. 25
12. A radiographic material according to claim 1 and substantially as described herein.
13. A radiographic material according to claim 1, such material incorporating a silver halide emulsion substantially corresponding with emulsion II or III in Example 1 thereof, and being substantially according to that Example or Example 2 or 3. 30
- 30 14. A method of producing a radiograph by direct exposure of a radiographic material to penetrating radiation, (i.e. without fluorescent screens) and processing such radiographic material, characterised in that the radiographic material used is a material according to any of claims 1 to 13.
- 35 15. A method according to claim 14, wherein the processing is performed in an automatic processing machine. 35

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