⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 555 897 A1**

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **93200139.9**

㉒ Date of filing: **20.01.93**

(51) Int. Cl.^{5}: **G03C 1/035**, G03C 5/16, G03C 1/83, G03C 1/30

㉚ Priority: **14.02.92 EP 92200420**

㊸ Date of publication of application:
18.08.93 Bulletin 93/33

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

(71) Applicant: **AGFA-GEVAERT naamloze vennootschap**
Septestraat 27
B-2640 Mortsel(BE)

(72) Inventor: **Raymond, Florens, c/o Agfa-Gevaert N.V.**
Die 3800, Septestraat 27
B-2640 Mortsel(BE)

(54) X-ray silver halide photographic material with suitable image tone and surface glare.

(57) The preparation of X-ray materials, especially suitable for non-destructive testing applications, is described. The emulsion layers of said material are comprising a mixture of chemically ripened cubic silver bromoiodide emulsion grains having a diameter of less than 0.30 µm and chemically ripened cubic silver chloride and/or silver chlorobromide and/or silver chlorobromoiodide emulsion grains having a diameter less than or at most 30% larger in size than said silver bromoiodide grains and being present in an amount of less than 20% by weight referred to the total amount of the coated silver halide crystals.

Applying this emulsion mixture into strongly hardened thin coated layers offers the advantage to get a suitable cold blue image tone with a suitable surface glare after development of the exposed material, especially if at least one non-migratory blue colouring agent is added to at least one of the hydrophilic colloid layers coated onto the blue coloured support.

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FIELD OF THE INVENTION

The present invention relates to photographic materials for industrial radiography having a preferred image tone.

BACKGROUND OF THE INVENTION

In the field of industrial radiography, especially for non-destructive testing applications, a reliable inspection of the materials to be investigated is only possible if the image obtained after developing has a good quality, i.e. sharpness and granularity.

Otherwise it is very important for the examiners that image tone and image glare are constant and acceptable to facilitate the observation. For non-destructive purposes the examiners are accustomed to cold black images, with preferably a slightly blue tone and sufficient glare.

In such X-ray photographic materials silver halide emulsion crystals with cubic silver bromoiodide grains are used as image-forming elements for the following reason. In order to achieve high film speed, which is an indispensible asset especially for direct-röntgen applications, efficient absorption of the exposure radiation is a prime condition. It has been shown empirically that for X-rays the mass absorption coefficient is proportional to a power of the atomic number Z as has been described in the "Encyclopaedic Dictionary of Physics" vol. 7. p. 787, eq. 10, Ed. J.Thewlis, Pergamom Press. Oxford 1957. This strongly disfavours e.g. the use of chloride ($Z=17$) compared to bromide ($Z=35$) or iodide ($Z=54$). Otherwise a cubic habit is favoured because of the volume effect of the silver halide crystal to get good absorption properties when exposing said crystals.

For globular silverbromoiodide crystals it has been established experimentally that by a reduction in grain size to a diameter smaller than 0.30 μm the image tone changes from pure black to brownish if the development is carried out in a typical processing sequence for industrial applications.

From recent patent literature it is well-known that "tabular" crystals show such a brownish image tone upon the processing of X-ray materials. Solutions for this problem have been found by the addition of chemical compounds as magenta dyes as disclosed in US-Patent 4,818,675, an anthraquinone dye and a quaternary ammonium salt as in Japanese Patent Application JN 89/029,838. Other solutions are found by the addition of sensitizing dyes added during the washing process in emulsion making as disclosed in JN-Patent Application 89/312,536, mercaptotetrazoles as in JN 86/170,739 or mercapto nitrogen-containing heterocyclic ring compounds as in JN 88/155,140, mercapto-alkylsulphonic acids or pseudo thiouronium intramolecular salt derivatives as in JN 89/017,044, dye-releasing redox-compounds generated by reductive cleavage as in JN 88/271,443, special-treated gelatins as in JN 88/180,944 and JN 88/180,945, polyacrylamide derivatives or its copolymers as in JN 89/091,132 and novel tone modifying agent precursors as ethylenically unsaturated compounds.

It is remarkable that for globular silver halide crystals the problem of undesirable image tone has not been mentioned and consequently there is no solution for it to be found in the patent literature, neither for medical X-ray, nor for industrial X-ray materials.

Otherwise it is well-known that matting agents are preferably present in hydrophilic layers of silver halide photographic materials to improve physical characteristics like transportability, sticking phenomena etc. A disadvantageous effect of these matte layers may be on the brilliance or lustre of the silver image.

To avoid turbidity in the matte layers of duplitized X-ray materials containing resorcinol, silica and poly-N-vinylpyrrolidone a solution is given in US-Patent 3,656,954 making use of sulphonated stilbene, triazine or naphtalene compounds. An improvement in surface glare (and adhesion properties) has been described in JN-Patent Application 87/275,240 for materials comprising specific grain size matting agent in the overcoat layer and in at least one other layer. An improvement of the brilliance of image silver can also be obtained by controlling the adjustment of the concentration of film hardener for silver halide photographic materials that comprise tabular grain emulsions with an average aspect ratio of more than 5 and with an average diameter between 0.2 and 0.6 μm as has been set forth in JN-Patent Application 87/286,839. Preferred hardeners are dimethylol urea and trimethylol melamine.

Also with relation to the phenomenon of surface glare it is remarkable that in the literature hardly any interest has been found for a silver halide photographic material comprising globular crystals and matting agents in at least one hydrophilic layer of said photograpic material.

OBJECTS OF THE INVENTION

A first object of the present invention is to provide a silver halide photographic material for industrial radiography which provides favourable image tone and surface glare characteristics to the developed film to be examined.

A second object of the invention is to provide an industrial photographic material with an excellent image quality, especially image sharpness, and good physical properties.

Other objects will become apparent from the description hereafter.

SUMMARY OF THE INVENTION

The above objects are accomplished by a photographic silver halide material for industrial radiography comprising a film support and on one or both sides thereof at least one silver halide emulsion layer which comprises a silver halide crystal mixture of silver bromoiodide and silver chloride and/or silver chlorobromide crystals and/or silver chlorbromoiodide crystals, the amounts of said chloride containing silver halide crystals being less than 20% by weight relative to the total amount of silver halide crystals present in the photographic material.

The silver chloride containing emulsion crystals, in addition to the original silver bromoiodide emulsion crystals, are chemically ripened emulsions having a cubic habit and a crystal diameter that is smaller or at most 30% larger in size than that of the globular silver bromoiodide emulsion crystals, said silver bromoiodide crystals having an average crystal diameter of 0.30 µm or less.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The silver halide emulsions formed according to the present invention comprise silver bromoiodide. Preferred silver bromoiodide emulsions comprise at most 10 mole% of iodide, preferably at most 3 mole% and still more preferably 1 mole%. Regular-shaped silver halide crystals and more particularly silver bromoiodide emulsions with cubic crystal habit as used in industrial radiographic materials are known to have good development characteristics with respect to high sensitivity. The parameter determining whether cubic or octahedral 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 U.S. Patent 3,821,002.

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 silver nitrate and potassium bromide, crystals of cubic form are obtained under conditions of low excess bromide concentration in the solution phase. A preferred embodiment of making the emulsions used according to the present invention involves the preparation of high-sensitive silver bromoiodide emulsions as these X-ray emulsions, by precipitation under double jet conditions. Although nowadays processes for the preparation of homogeneous silver halide emulsions make use of special control devices to regulate the form of the resulting silver halide crystals, said form mainly being determined by the pAg value and temperature in the reaction vessel, the silver ion concentration can be kept constant during the precipitation by the use of a special inlet technique as described in Research Disclosure, Item 10308.

The average grain-size of the silver halide emulsions made according to the present invention is preferably situated between 0.1 and 0.3 µm. Particle size of silver halide grains 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.

To obtain a reproducable crystal size especially the flow rate and concentration of the solutions, the temperature and pAg have to be adjusted very carefully. Grain-growth restrainers or accelerators may be added from the start or during the preparation of the emulsion crystals. Depending on the initial conditions during precipitation, monodispersed emulsions can be prepared as is preferable for this invention. Monodispersed emulsions in contrast to heterodispersed emulsions have been 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%.

Silver halide grains having a very narrow grain-size distribution can thus be obtained by strictly 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, a mixture of potassium bromide and potassium iodide, 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 Application 392,092.

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 phenomenon, which gives rise to the broadening of the silver halide crystal distribution.

In accordance with the present invention the emulsions added to the silver bromoiodide emulsions mentioned before are emulsions containing silver chloride crystals, silver chlorobromide or silver chlorobromoiodide crystals preferably containing up to 25 mole% of bromide ions and up to 1 mole% of iodide ions.

For the preparation of gelatino silver chloride, chlorobromide or chlorobromoiodide emulsions used in accordance with the present invention conventional lime treated or acid treated gelatin can be used. The preparation of such gelatin types has been described in e.g. "The Science and Technology of Gelatin", edited by A.G. Ward and A. Courts, Academic Press 1977, page 295 and next pages. The gelatin can also be an enzyme-treated gelatin as described in Bull. Soc. Sci. Phot. Japan, N° 16, page 30 (1966). Before and during the formation of the silver halide grains the gelatin concentration is kept from about 0.05 % to 5.0 % by weight in the dispersion medium. Additional gelatin is added in a later stage of the emulsion preparation, e.g. after washing. The gelatin to silver halide ratio then ranges from 0.3 to 1.2. Although the precipitation in connection with the present invention can be principally performed by one double jet step it is possible to perform a sequence of a nucleation step and at least one growth step. Of the total silver halide precipitated preferably 0.5 % to 5.0 % is added during said nucleation step which consists preferably of an approximately equimolecular addition of silver and halide salts. The rest of the silver and halide salts is added during one or more consecutive double jet growth steps. The different steps of the precipitation can be alternated by physical ripening steps. During the growth step(s) an increasing flow rate of silver and halide solutions is preferably established, e.g. a linearly increasing flow rate. Typically the flow rate at the end is about 3 to 10 times greater then at the start of the growth step. These flow rates can be monitored by e.g. magnetic valves. There can be a heterogeneous or homogeneous distribution of the silver halide used over the whole volume of the silver halide crystals. In the latter case the composition of the halide solution remains unchanged during the whole precipitation. Within the scope of this invention an amount of not more than 25 mole% of bromide ions and an amount of not more than 1 mole% of iodide ions may be built into the silver halide crystals homogeneously. In order to get a homogeneous silver halide crystal distribution after precipitation it is recommended that before the start and during the different stages of the precipitation the pAg is maintained between 105 and 85 mV during the nucleation step and preferably between 90 and 65 mV during the growth step and pH is maintained between 5.2 and 5.8 preferably between 5.6 and 5.8. When using conventional precipitation conditions chloride rich silver halide emulsion grains show a cubic morphology with (100) crystal faces offering better developing characteristics than other crystallographic forms, as e.g. octahedral, rhombic dodecahedral or tabular silver chloride crystals, which require the use of so-called "growth modifiers" or "crystal habit modifiers". The silver chloride, chlorobromide or chlorobromoiodide grains used in accordance with the present invention preferably have an average grain size from 0.10 to 0.40 μm.

Once the grains have reached their ultimate size and shape, the emulsions are generally washed to remove the by-products of grain-formation and grain-growth. In order to remove the excess of soluble salts washing is applied at a pH value which can vary during washing but remains comprised between 3.7 and 3.0 making use of a flocculating agent like polystyrene sulphonic acid. The emulsion may be washed by diafiltration by means of a semipermeable membrane, also called ultrafiltration, so that it is not necessary to use polymeric flocculating agents that may disturb the coating composition stability before, during or after the coating procedure. Such procedures are disclosed e.g. in Research Disclosure Vol. 102, Oct. 1972, Item 10208, Research Disclosure Vol. 131, March, Item 13122 and Mignot US-Patent 4,334,012. Preferably, at the start of the ultrafiltration, there is no pH and pAg adjustment as pH and pAg are maintained at the same level as at the end of the preceding precipitation without any adjustment stage.

In accordance with the present invention, the emulsions 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 Application 91201426.3.

Coagulation techniques using acid-coagulable gelatin derivatives have been described e.g. in U.S. Patent Specifications 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 United States Patent Specifications referred to above. Particularly suitable are phthaloyl gelatin and N-phenylcarbamoyl gelatin.

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, where upon the coagulum is washed out once or several times.

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, recoagulating by addition of an acid to reduce the pH to the coagulation point and subsequently removing the supernatant liquid. This redispersion and recoagulation operation may be repeated as many times as is necessary.

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, 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 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.

The light-sensitive silver bromoiodide and silver chloride containing emulsions are seperately chemically sensitized with a sulphur and gold sensitizer. This can be done as described i.a. in "Chimie et Physique Photographique" by P. Glafkides, in "Photographic Emulsion Chemistry" by G.F. Duffin, in "Making and Coating Photographic Emulsion" by V.L. Zelikman et al, and in "Die Grundlagen der Photographischen Prozesse mit Silberhalogeniden" edited by H. Frieser and published by Akademische Verlagsgesellschaft (1968). As described in said literature 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. Gold sensitization occurs by means of gold compounds. In addition small amounts of compounds of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd or Pt can be used. The emulsions can 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.

After chemical ripening the silver bromoiodide crystals and the silver chloride containing emulsions can be added separately to the vessel containing the coating solutions in weight ratio amounts varying from 70/30 to 98/2.

In accordance with the present invention compounds 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 supplementary 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, JA-Appl. 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, which are giving an unsatisfactory result if added as the sole stabilizing agent and are therefore combined with other stabilizers belonging to the classes of stabilizers already mentioned. On the other hand mercury salts and other metal-salts that can be used as fog-inhibiting compounds such as cadmium salts and related compounds described in Research Disclosure N° 17643 (1978), Chapter VI, should be avoided for reasons of ecology.

The ratio of gelatin to silver halide (expressed as silver nitrate) in the silver halide emulsion layers of the photographic material according to the present invention is comprised between 0.3 and 1.2, preferably between 0.6 and 1.1.

The gelatin binder of the photographic elements according to the present invention 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 or di-(vinyl-sulphonyl)-methane, aldehydes e.g. formaldehyde, glyoxal, and glutaric aldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts as disclosed in US 4,063,952 and with the onium compounds as disclosed in European Patent Application No 90.201850.6

Hardening is to such an extent that when the photographic material is rinsed at the end of the processing cycle, just before drying, at most 2.5 g of water is absorbed per gram of gelatin, as will become apparent from the examples, given hereinafter.

The photographic elements under consideration may further comprise various kinds of surface-active agents in the photographic emulsion layer and/or in at least one other hydrophilic colloid layer. Preferred surface-active coating agents are compounds containing perfluorinated alkyl groups.

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

The photographic element of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, 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.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene 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.

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...

Suitable additives for improving the dimensional stability of the photographic element 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, Alpha-Beta-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

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.

In general, the average particle size of spacing agents is comprised between 0.2 and 10 µm. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents usually are removed therefrom in an alkaline processing bath. Suitable spacing agents can be made 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.

The photographic element can comprise an antistatic layer e.g. to avoid static discharges during coating, processing and other handlings of the material. Such antistatic layer can be an outermost coating or 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 and the like.

The photographic material according to the present invention is preferably a duplitized material having on both sides of the film support emulsion layers. Both emulsion layers are overcoated with an antistress top layer. For industrial radiography the silver halide emulsion layer(s) preferably comprise an amount of silver halide corresponding to between 5 and 15 g of silver per square meter and per side.

The support of the photographic material in accordance with the present invention may be a transparent resin, preferably a blue coloured polyester support like polyethylene terephtalate. The thickness of such organic resin film is preferably about 175 µm. The support is provided with a substrate layer at both sides to have good adhesion properties between the emulsion layer and said support.

The photographic material can be image-wise exposed by means of an X-ray radiation source the energy of which, expressed in kV, depends on the specific application. Another typical radiation source is a radioactive Co^{60} source. To reduce the effect of scattering radiation a metal screen, usually a lead screen, is used in combination with the photographic film. Besides the generation of secondary electrons makes the sensitivity to enhance.

For processing, preferably an automatically operating apparatus is used provided with a system for automatic replenishment of the processing solutions as will be clearly illustrated in the examples.

The developer solution according to the invention has to be replenished not only for decrease of the liquid volume due to cross-over into the next processing solution but also for pH-changes due to oxidation of the developer molecules. This can be done on a regular time interval basis or on the basis of the amount of processed film or on a combination of both. The development step can be followed by a washing step, a fixing solution and another washing or stabilization step. Finally after the last washing step the photographic material is dried. A further fine-tuning of the absorption spectrum of the the material as obtained after this processing may be obtained by the addition of suitable non-migratory dyes to the subbing layer, the emulsion layer(s) or the topcoat layer at both sides of the support. A blue coloured dye is especially recommended within the scope of this invention.

The following examples will fully illustrate the invention described hereinbefore.

EXAMPLES

Example 1

Emulsion A

A gelatino silver iodobromide X-ray emulsion comprising 99 mole % of silver bromide and 1 mole % of silver iodide was prepared in the following way. An aqueous solution containing 11 grams of methionin was added to the reaction vessel containing 1550 ml of a 3 % by weight aqueous solution of gelatin at 45 °C. Into said reaction vessel a solution of 2000 ml of an aqueous 1.5 molar solution of potassium bromide and a solution of 2000 ml of an aqueous 1.5 molar solution of silver nitrate were introduced at constant rate of 86 ml/min under vigorously stirring conditions. During precipitation the pAg value was adjusted to and maintained at a value corresponding to an E.M.F. of +20 mV as referred to a silver/saturated calomel reference electrode. In this way homogeneous and regular silver halide grains having a crystal diameter of 0.19 µm were obtained,

At the end of the precipitation step, the emulsion was coagulated by adding polystyrene sulphonic acid acting as a flocculating agent after adjustment of the pH value of the emulsion in the reaction vessel to 3.5 with sulphuric acid. After rapid sedimentation of said silver halide emulsion the supernatant liquid was decanted. To remove the water-soluble salts from said flocculate demineralized water of 11 ° C was added under controlled stirring conditions followed by a further sedimentation and decantation. This washing procedure was repeated until the emulsion was sufficiently desalted. Thereafter the coagulum was redispersed at 45 ° C in water after the addition of a sufficient amount of gelatin to obtain a ratio of gelatin to silver nitrate of 0.4. The pH-value was adjusted to 6.5 and pAg to a value of +70 mV as referred to the silver/saturated calomel electrode.

Chemical sensitization of said emulsion was performed by the addition of a sulphur and gold sensitizer and digestion at 50 ° C to the point where the highest sensitivity was reached for a still acceptable fog level.

Emulsion B.

A gelatino silver chlorobromide emulsion comprising 90 mole % of silver chloride and 10 mole % of silver bromide was prepared in the following way. The silver halide was precipitated in an aqueous solution of gelatin at 40 ° C by the addition, making use of the double-jet technique, of an aqueous solution of silver nitrate and an aqueous solution of chloride and bromide salts in the right mixture to obtain the composition mentioned previously. The silver halide crystals were physically ripened in a conventional way until the desired grain size of 0.16 µm was reached, stopping said physical ripening step by coagulation of said silver halide emulsion, acidifying to a pH value of 3.0 of the emulsion to which polystyrene sulphonic acid was added before. Washing procedures were following as for emulsion A, whereafter gelatin was added to obtain a weight ratio of gelatin to silver halide, expressed as silver nitrate, of 0.5. The emulsion was chemically sensitized by the addition of a sulphur and gold sensitizer and digestion was followed at 45 ° C until the optimum relation between sensitivity and fog was obtained. Silver halide crystals had an average diameter of 0.16 µm.

Emulsion C.

Emulsion C, containing 83.6 mole % of silver chloride, 16 mole % of silver bromide and 0.4 mole % of silver iodide, was prepared in the same way as emulsion B. The silver halide crystals of said emulsion had an average crystal diameter of 0.3 µm.

Film 11 (comparative sample).

As a comparative example this film was coated with emulsion A at both sides of a blue polyethylene terephtalate support having a thickness of 175 µm. At both sides silver halide emulsion crystals and gelatin were coated onto the support in amounts of 10.5 g, expressed as silver nitrate, per square meter and 8.9 g respectively. Before coating stabilizers as 5-methyl-7-hydroxy-5-triazolo-[1,5-a]-pyrimidin and 1-phenyl-5-mercaptotetrazol were added to the emulsion. Both emulsion layers were covered with a protective layer of 1.4 grams of gelatin per square meter and hardened with di-(vinyl-sulphonyl)-methane.

Said coated and dried film was exposed according to ISO 7004 with a 235 kV radiation source with a copper filter of 8 mm thickness.

The exposed radiographic film was developed, fixed, rinsed and dried in an automatic machine processing cycle of 8 minutes. The film was run in a Structurix NDT-1 machine marketed by Agfa-Gevaert and developed at 28 ° C in the commercially available Agfa-Gevaert NDT-developer G135 followed by a fixation step using Agfa-Gevaerts commercial G335 fixer.

Film 12.

Film 12 was coated in the same way as film 11, the difference with said previous film 11 being realized by admixture of emulsion A and emulsion B, in an amount that corresponds to 95 % by weight of the total amount of silver halide, expressed as silver nitrate for emulsion A and 5% for emulsion B. Amounts of silver nitrate, gelatin and degree of hardening were the same for film 12 and film 11.

Film 13.

Film 13 was coated in the same way as film 12, the only difference being the replacement of emulsion B by emulsion C.

Sensitometric results after exposure and processing according to the procedures described for Film 11 are listed in Table I. The values given for the sensitivity S in Table I are relative speed values with respect to reference film 11, the speed of which was given a value of 100. Fog F includes the density of the blue support. Contrast C is the average gradient of the segment of the curve linking two points between densities 1.5 and 3.5. The image tone is a result of the colour of the developed silver. The image tone may vary from warm- or brown- to blue-black. For non-destructive purposes a blue-black image tone is preferred. A visual comparison of image tone I.T. in the film samples is given in Table I : the lowest number is given to the sample having the better the image tone.

Table I

Film	Emulsion	F	S	C	I.T.
11	A	0.134	100	6.34	3
12	A+B	0.139	112	6.13	1
13	A+C	0.140	110	6.21	2

The results listed in Table I clearly illustrate the importance of the presence of the silver chloride or silver chlorobromide emulsion crystals to improve image tone.

Example 2.

Film 21.

A mixture of emulsions A and B was prepared and coated in the same way as for film 12 of example 1. Di-(vinyl-sulphonyl)-methane was used as a hardener.

Film 22.

Same as for film 21 but only 75 % of the amount of di-(vinyl-sulphonyl)-methanewas used.

Film 23.

Same as for film 21 but only 50 % of the amount of di-(vinyl-sulphonyl)-methanewas used.

Film 24.

Same film as film 21 but the emulsion was hardened with formaldehyd.

Film 25.

Same film as film 24 but only 66 % of the amount of formaldehyd was used.

The degree of hardening is expressed by the amount of water in grams per square meter absorbed by the film after rinsing at the end of the processing just before drying. Data given in Table II correspond with those in Table I, except for the degree of hardening, mentioned previously, that is given additionally in Table II.

Table II

Film	Emulsion	F	S	C	I.T.	g H_2O/m^2
21	A+B	0.141	100	6.41	1	37.29
22	A+B	0.141	102	6.62	3	41.84
23	A+B	0.143	107	6.74	5	43.60
24	A+B	0.141	102	6.34	2	40.04
25	A+B	0.142	105	6.62	4	43.44

Results listed in Table II show that the degree of hardening has an important effect on image tone: the higher the degree of hardening the better the image tone.

Example 3.

Film 31.

A mixture of emulsion A and B was prepared and coated in the same way as film 12 of example 1. Di-(vinyl-sulphonyl)-methane was used as a hardener. The weight ratio of gelatin to silver halide, expressed as silver nitrate, was 0.85. This weight ratio is called "GESI" hereinafter.

Film 32.

Same as for film 31 but the weight ratio of gelatin to silver halide, expressed as silver nitrate, was 0.98.

Film 33.

Same as for film 31 but the ratio of gelatin to silver halide, expressed as silver nitrate, was 1.10.

Table III gives the summary of the same data as in Table II with in addition the data of weight ratio of gelatin to silver halide, called GESI. The amount of silver halide is expressed as the equivalent amount of silver nitrate.

Table III

Film	Emulsion	F	S	C	I.T.	GESI	g H_2O/m^2	g gel./m^2	g H_2O/g gel.
31	A + B	0.142	100	6.47	1	0.85	30.44	20.6	1.48
32	A + B	0.142	95	6.63	2	0.98	35.12	23.4	1.50
33	A + B	0.143	93	6.49	3	1.10	39.31	25.9	1.51

The results listed in Table III show that the ratio of gelatin to silver halide, expressed as silver nitrate, has a noteworth effect on image tone. The lower that ratio, the better the image tone for the same amount of water absorption per square meter and per gram of gelatin as is the case in example 3.

Example 4.

Film 41.

Emulsion A was prepared and coated in the same way as for film 11 of example 1. Di-(vinyl-sulphonyl)-methane was used as a hardener.

Film 42.

Film 42 was coated in the same way as for film 41 but a mixture of emulsion A and emulsion B was used in amounts of respectively 95 % and 5 % by weight of the total amount of silver halide, expressed as silver nitrate.

Film 43.

Same as for film 42 but emulsions A and B were respectively in amounts of 90 % and 10 % by weight of the silver halide, expressed as silver nitrate.

Film 44.

Same as for film 42 but emulsions A and B were used in amounts of 80 % and 20 % by weight.

Film 45.

The same coating as for film 41, except for the addition of a gelatinous dispersion of blue coloured dye, known as "CERESBLAU RR", c.i. solvent blue 97, trademarked product of BAYER AG. Said blue coloured dye was coated in a total amount of 560 mg/m^2 and added to the emulsion just before coating.

Film 46.

Same film as film 45, except for the double-side coated amount of the blue coloured dye of 1120 mg/m^2.

Film 47.

Film 47 was prepared and coated in the same way as film 42, except for the addition of the blue coloured dye of film 45 in an amount of 1120 mg/m^2 to the emulsion just before coating.

Film 48.

Film 48 was prepared and coated in the same way as film 43, except for the addition of the blue coloured dye of film 45 in an amount of 1120 mg/m^2 to the emulsion just before coating.

Film 49.

Film 49 was prepared and coated in the same way as film 48, except for the amount of only 75 % of the amount of di-(vinyl-sulphonyl)-methane used for film 48.

Film 50.

Film 50 was prepared and coated in the same way as film 48 but with a ratio of gelatin to silver halide, expressed as silver nitrate, of 1.1 instead of 0.85.

In Table IV the results are summarized as in table III. Additionally the amount of the blue coloured dye CERESBLAU RR per square meter is given and the percentage of hardener added. The ratio of the amounts of emulsion A and B in the mixture are also given.

Table IV

Film	Emulsion	F	S	C	I.T.	GESI	g H_2O/m^2	dye/m^2	% hardener
41	A	0.144	100	6.58	8	0.85	32.38	- - -	100
42	A + B (95/5)	0.150	105	6.43	7	0.85	32.61	- - -	100
43	A + B (90/10)	0.149	102	6.24	6	0.85	32.38	- - -	100
44	A + B (80/20)	0.149	100	5.82	4	0.85	32.86	- - -	100
45	A	0.161	98	6.50	5	0.85	32.45	560	100
46	A	0.181	100	6.50	3	0.85	31.79	1120	100
47	A + B (95/5)	0.181	105	6.38	2	0.85	32.78	1120	100
48	A + B (90/10)	0.187	102	6.19	1	0.85	32.14	1120	100
49	A + B (90/10)	0.192	105	6.31	3	0.85	35.36	1120	75
50	A + B (90/10)	0.188	98	6.20	4	1.10	40.43	1120	100

The results listed in Table IV clearly illustrate the importance of the presence of a silver chloride containing emulsion, partially replacing silver bromoiodide emulsion crystals to improve image tone. An additional, but also very important improvement, can be attained by the simultaneous addition of silver chloride containing crystals and a blue coloured dye, said improvement being enhanced by increasing the degree of hardening and lowering the ratio of gelatin to silver halide. A very clear illustration of this statement is given by film coating numbers 47 and 48 in Table IV.

Claims

1. A photographic silver halide material for industrial radiography comprising a film support and on one or both sides thereof at least one silver halide emulsion layer characterised in that each silver halide emulsion layer comprises a mixture of chemically ripened cubic monodisperse silver bromoiodide and chemically ripened cubic monodisperse silver chloride and/or silver chlorobromide and/or silver chlorobromoiodide emulsion crystals.

2. A photographic silver halide material according to claim 1 wherein said chemically ripened monodisperse silver bromoiodide emulsion crystals are present in an amount of at least 80 % by weight expressed as silver and said chemically ripened silverchloride and/or silver chlorobromide and/or silverchlorobromoiodide emulsion crystals are present in an amount of 20% by weight or less.

3. A photographic silver halide material according to claims 1 or 2 wherein said chemically ripened silver bromoiodide emulsion crystals have a crystal diameter of 0.10 to 0.30 μm and said chemically ripened silverchloride and/or silver chlorobromide and/or silver chlorobromoiodide emulsion crystals have a crystal diameter that is smaller than or at most 30 % larger in size than said silver bromoiodide emulsions.

4. A photographic material according to any of claims 1 to 3 wherein said silver chloride and/or silver chlorobromide and/or chlorobromoiodide emulsion(s) has(have) homogeneously divided halide ions over its(their) crystal volume.

5. A photographic material according to any of claims 1 to 4 wherein the chloride-containing emulsion(s) has(have) a chloride content of at least 75 mole%, a bromide content of up to 25 mole% and an iodide content of up to 1 mole%.

6. A photographic material according to any of claims 1 to 5 wherein said material is a double-coated radiographic material having a silver halide emulsion layer on both sides of the support.

7. A photographic material according to any of claims 1 to 6 wherein said material has a ratio by weight of gelatin to silver halide, expressed as silver nitrate from 0.3 to 1.2 and has been hardened to such an extent that after rinsing at the end of a processing cycle it absorbs less than 2.5 grams of water per gram of gelatin,

8. A photographic material according to claim 7 wherein the binder has been hardened with di-(vinylsulphonyl)-methane

9. A photographic material according to any of claims 1 to 8 wherein at least one blue colouring non-migratory dye is present in at least one of the hydrophilic colloid layers on said support.

10. A photographic material according to claim 9 wherein the support is a blue coloured support and said blue colouring dye(s) is(are) present in an amount of up to 1200 mg/m^2.

11. A photographic material according to any of claims 9 and 10 wherein at least one of said blue colouring dyes is CERESBLAU RR, c.i. solvent 97, trademarked by BAYER AG.

12. A photographic material according to any of claims 9 to 11 wherein said blue colouring agent(s) is(are) present in the form of a solid particle dispersion.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0139

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 063 962 (KONISHIROKU PHOTO INDUSTRY COMPANY LTD) * page 13, line 25; claims 1-10 * * page 14, line 23 - page 15, line 2 *	1-12	G03C1/035 G03C5/16 G03C1/83 G03C1/30
Y	PATENT ABSTRACTS OF JAPAN vol. 13, no. 43 (P-821)(3391) 31 January 1989 & JP-A-63 239 434 (FUJI PHOTO FILM COMPANY LTD.) 5 October 1988 * abstract *	1-5	
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 211 (P-594)(2658) 9 July 1987 & JP-A-62 031 846 (KONISHIROKU PHOTO INDUSTRY COMPANY LTD) * abstract *	1-5	
Y	EP-A-0 276 566 (EASTMAN KODAK COMPANY) * page 10, line 53 - line 54; claims 1-10 *	6-12	
Y	DATABASE WPI Section Ch, Week 8007, Derwent Publications Ltd., London, GB; AN 80-11740C & JP-A-55 000 734 (DIAFOIL K.K.) * abstract *	10,11	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 MAY 1993	BUSCHA A.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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