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27  
B-2640 Mortsel(BE)**(54) **Method of preparing a silver halide light-sensitive photographic material.**

(57) A method of preparing a silver halide light-sensitive photographic material incorporating layers of emulsions precipitated in colloidal silica serving as a protective colloid. The silver halide emulsion either or not being chemically sensitized in the presence of a spectral sensitizer is less subjected to pressure phenomena, even for thin coated layers, highly sensitive and rapidly processable. Its higher coverage power after development permits the coating of less silver, resulting in a customer-friendly consumption of less chemicals.

**EP 0 528 476 A1**

## FIELD OF THE INVENTION

The present invention relates to a silver halide light-sensitive photographic material which is highly sensitive, rapidly processable, less subjected to pressure phenomena and which has a high coverage power.

## BACKGROUND OF THE INVENTION

In recent years, the consumption of silver halide photographic light-sensitive materials has been and is increasing steadily. Accordingly, the processing number of silver halide photographic materials increases, leading to the demand for even more rapid processing.

The above-mentioned tendency is also seen in the field of light-sensitive X-ray materials, e.g. medical radiographic films. The significant increase in the number of diagnosis due to the strict observation of periodical medical checks and the increase in the medical inspection items to make the diagnosis even more correct leads to the increase in the number of radiographing films. On the other hand, the necessity to inform the medical examiners as soon as possible makes that there are strong demands for more rapid processing than ever before in order to immediately provide the processed results for the diagnosis. Particularly in the midst of a surgical operation, and the like, the viewing in no time of the finished radiographic image is a necessity!

In order to meet the above wishes of the medical field, it is necessary to speed up the processing of X-ray films as well as to promote the automation of the diagnostic procedure, including radiographing and transportation.

One of the ways to make a film suitable to rapid processing, especially with a view to reach an adequate sensitivity and image density, is to reduce the amount of gelatin. However, this interference gives rise to various other problems as the silver halide crystals in the coated layers are less protected against stress or pressure phenomena. As a result, marks or streaks tend to appear where the film is rubbed with another film or with other materials, e.g. in an automatic processor. Scratch darkening may appear after development so that the parts that have been rubbed show a higher density than unimpaired parts. Opposite to this situation, a lowering of the density may appear when the film has been bent or folded on account of being handled by an operator before imagewise exposure and development: in this case the so-called pressure desensitization is deteriorating the image and leading to erroneous diagnosis. Taking into account the more difficult coating procedures the concept of lower gelatin charges doesn't seem to be attractive.

From the viewpoint of ecology, it is in addition an engagement of the manufacturer of films and developers to reduce environmental pollution, due to the use of his system, to a minimum level. So it should be recommended to reduce the consumption of chemicals as much as possible. However it is not always self-evident to reduce the amount of e.g. the coated silver halide crystals in the emulsion layers without coming into conflict with specific demands concerning sensitometry and image quality.

In order to meet the demands mentioned above a number of commonly well-known proposals have been formulated such as the improvement of physical properties of the film or a change in the composition of the developer, fixer etc., providing more customer-friendly chemicals, leading to better treatable by-products. However most of them are affecting the photographic characteristics so that new ways had to be explored.

## OBJECTS OF THE INVENTION

It is an object of the present invention to provide a silver halide light-sensitive photographic material combining the characteristics of high sensitivity in rapid processing and the capability of having a good resistance to pressure sensitivity, whatever the source might be. In addition it is an object to provide developed silver halide crystals of an excellent coverage power, so that emulsion layers can be coated with less silver which consequently leads to less consumption of chemicals during development of the material, less silver recovery and less by-products afterwards.

Other objects will become apparent from the description hereinafter.

## SUMMARY OF THE INVENTION

From a range of experiments it has been found that it is possible to produce materials, satisfying the properties mentioned above, by coating emulsion layers from silver halide emulsions the silver halide of

which has been precipitated in colloidal silica as has been described e.g. in EP 0392092.

In accordance with the present invention a photographic material satisfying the above objects and comprising a support and one or more silver halide emulsion layers is prepared by coating a support with one or more hydrophilic colloid layers including at least one layer of a silver halide emulsion prepared by the steps of:

- precipitating silver halide in colloidal silica as a protective colloid in the absence of any polymeric compound(s) capable of forming hydrogen bridges with colloidal silica such as gelatin,
- desalting the emulsion and redispersing the silver halide in the presence of gelatin,
- chemically ripening the silver halide,
- spectrally sensitizing the silver halide emulsion if desired, and
- finishing the emulsion ready for coating so that in said emulsion ready for coating the ratio of gelatin to silver halide expressed as silver nitrate is comprised between 0.05 and 0.40, preferably between 0.15 and 0.30, and the ratio of silica to silver halide expressed as silver nitrate is comprised between 0.01 and 2.0, preferably between 0.02 and 1.0.

## DETAILED DESCRIPTION OF THE INVENTION

As the starting point after precipitation of the silver halide is a gelatin to silver nitrate ratio of zero, the ratio by weight of gelatin over silver nitrate is adjusted by adding an adapted amount of gelatin at the stage of or after redispersing the desalted emulsion. The ratio of silica to silver halide is determined at the stage of precipitation and/or by further addition of silica at the redispersion stage or later. The most remarkable difference between silver halide emulsions being precipitated in colloidal silica and those prepared in gelatinous medium is the fact that colloidal silica is effectively surrounding the silver halide crystal, preventing the adsorption of a competitive protective colloid like gelatin, resulting in a weaker inhibition of the development. By the precipitation in colloidal silica and the selection of the particular ratios of silica and gelatin to silver halide the emulsions are very suitable in rapid processing systems.

In addition thereto an increase of the coverage power, defined as the density obtained per weight unit of developed silver halide, could be realised. This effect is probably due to the formation of thin, homogeneously divided silver filaments being generated during the rapid development process. With less silver halide the same maximum density as for comparative emulsions being precipitated in gelatin can be obtained.

A further unexpected effect of the present invention is the better resistance of the coated material to pressure phenomena. Emulsion layers in accordance with the present invention, especially thin emulsion layers are showing remarkable improvements concerning both resistance to stress and rapid processability compared to conventional emulsions prepared in gelatinous medium. As the ratio of weight of gelatin to silver halide decreases the effect is more pronounced and is probably a result of the protective action of the adsorbed silica to the silver halide crystal surface.

According to the present invention the photographic silver halide can be precipitated by mixing the halide and silver solutions in the colloidal silica medium under partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide grains to be used in practising this invention may be prepared by applying the orderly mixing, inversely mixing, double jet, conversion, core/shell method or the like. Epitaxial depositions, whether or not directed by so called "site-directors", may be useful.

Suitable preparation methods are described e.g. by T.H. James in "The Theory of the Photographic Process", 4th edition (Macmillan, 1977); P. Glafkides in "Chimie et Physique Photographique", Paul Montel, Paris (1967), by G.F. Duffin in "Photographic Emulsion Chemistry", the Focal Press, London (1966), and V.L. Zelikman et al. in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

The average size of the silver halide grains used in accordance with the present invention may range from 0.01 to 7  $\mu\text{m}$ , preferably from 0.3 to 3  $\mu\text{m}$ . The size distribution of the silver halide particles of the photographic emulsions may be homodisperse or heterodisperse. Homodisperse distributions are obtained when 95 % of the grains have a size that does not deviate for more than 30 % from the average grain size. In preparing those emulsions the supply of silver and halide ions may be so as to have a growth rate of the grains which is gradually and continuously increasing, never exceeding the critical growth rate in order to avoid the production and growth of newly created nuclei, nor being too low, resulting in the dissolution of the existing finest grains. This critical growth rate varies according to a lot of parameters, e.g. temperature, pH, pAg, the grain size, crystal habit and halide composition of the crystals, the dilution of the emulsion in the reaction vessel, etc.

The silver halide particles of the photographic emulsions according to the present invention may have a regular crystalline form, e.g. cubic or octahedral or a transition form. Also an irregular crystalline form such as a spherical form or a tabular form may be obtained. Otherwise the emulsion crystals may have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

The silver halide grains may also have a multilayered grain structure. The crystals may be doped with whatever a dope, as e.g. with  $\text{Rh}^{3+}$ ,  $\text{Ir}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ . There are no restrictions concerning the halide composition: chloride, bromide, iodide and any combination may be used. Preferred are silver bromide, silver bromoiodide, silver chloride, silver chlorobromide and silver chlorobromoiodide emulsions.

Two or more different, separately formed silver halide emulsions may be mixed and used in accordance with the present invention.

During precipitation grain growth restrainers or accelerators may be added. Although there is no need for grain growth restrainers in order to prepare ultrafine silver halide crystals it may be useful to add one e.g. when the temperature is high in the reaction vessel. When preparing ultra fine grains in the presence of growth restrainers, as e.g. phenylmercaptotetrazoles, it should be noted that these restrainers strongly adsorb to the silver halide crystal surface and that it is very difficult, if not impossible, to remove them by washing procedures so that their influence on photographic properties persists after coating. Therefore this is preferably avoided. Ultra fine emulsions can act as seed crystals in preparation techniques, making use of Ostwald ripening or recrystallisation steps.

The usual silica sols are suitable for the process according to the invention. Suitable silica sols are commercially available such as the "Syton" silica sols (a trademarked product of Monsanto Inorganic Chemicals Div.), the "Ludex" silica sols (a trademarked product of duPont de Nemours & Co., Inc.), the "Nalco" and "Nalcoag" silica sols (trademarked products of Nalco Chemical Co) and the "Kieselsol, Types 100, 200, 300, 500 and 600" (trademarked products of Bayer AG).

The light-sensitive silver halide emulsion prepared according to the present invention can be chemically sensitized as described i.a. in the above-mentioned "Chimie et Physique Photographique" by P. Glafkides, in the above-mentioned "Photographic Emulsion Chemistry" by G.F. Duffin, in the above-mentioned "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 chemical 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 rhodanines. The emulsions can be sensitized also by means of gold-sulphur ripeners or by means of reductors e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. Chemical sensitization can also be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitization methods or a combination thereof can be used. The chemical sensitization is generally carried out under well-defined conditions of pH, pAg, temperature, gelatine, silver halide and sensitizer concentration until sensitivity and fogging are both optimal. Especially in the case of emulsion crystals with a high internal sensitivity, the surface has to be chemically sensitized because otherwise the sensitivity is not sufficient in a surface developer.

It is even possible to add the chemical ripening agents during or at the end of the precipitation into the reaction vessel and to complete the chemical ripening before starting the coagulation procedure. An advantage of this embodiment is that an excess of chemical ripening agents is eliminated so that negative influences on the stability of the material during preservation are substantially reduced.

In a preferred embodiment of the invention, the silver halide crystals are chemically sensitized in the presence of a spectral sensitizer, which results in an improved relationship between fog and sensitivity especially in short development times. So it is specifically recommended in this invention that spectral sensitization should be started concurrently with chemical sensitization, even entirely preceding chemical sensitization as has been mentioned in Research Disclosure 22534, p. 28, including also alternative procedures such as introducing a portion of sensitizing dye prior to chemical sensitization and the remaining portion at the end, being suggested by Locker et al. USP 4225666. In a preferred embodiment a blue spectrally sensitizing dye is added before the addition of the chemical ripening agents and/or during chemical sensitization. Spectral sensitization can be improved by chemical sensitization methods as has been described in U.S. Patent Nos. 3.917.485 and 3.966.476.

Chemically ripening in the presence of spectral sensitizers has been described in F. Hamer "The Cyanine Dyes and Related Compounds", 1964, and in Ullmanns Encyclopädie der Technischen Chemie, 4th Edition, Vol. 18, pages 431 et seq and Research Disclosure No. 17643, Section III. Spectral sensitizers may be added before or after the addition of the chemical ripening agents and may even portionwise be added at different stages during the process. Besides these compounds, acting as sensitizing aids,

compounds as azaindenes, azapyridines or azapyrimidines, the latter compounds being known as stabilizers, are reducing fog and increasing sensitivity in such emulsions as well. Descriptions of these effects have been given in U.S. Patent Nos. 2,131,038, 3,411,914 and 3,554,757, in JP-A-58-126526 and in G.F. Duffin, *Photographic Emulsion Chemistry*, p. 138-143.

In a common embodiment the light-sensitive silver halide emulsions of the invention can also be spectrally sensitized prior to coating with methine dyes such as those described by F.M. Hamer in the above-cited "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly valuable dyes are those belonging to the cyanine dyes, merocyanine dyes, complex merocyanine dyes. Other dyes, which per se do not have any spectral sensitization activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitization effect when they are incorporated together with said spectral sensitizing agents into the emulsion. Suitable supersensitizers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described in e.g. US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described in e.g. US-A 2,933,390 and US-A 3,635,721, aromatic organic acid/formaldehyde condensation products as described in e.g. US-A 3,743,510, cadmium salts, and azaindene compounds.

To the silver halide emulsion prepared in accordance with the present invention may be added compounds preventing the formation of fog or stabilizing the photographic characteristics during the production or storage of photographic elements or during the photographic treatment thereof. Many known compounds can be added as fog-inhibiting agent or stabilizer to the silver halide emulsion. Suitable examples are i.a. the heterocyclic nitrogen-containing compounds such 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-Apl. 75-39537, and GB-A 1,500,278, and 7-hydroxy-s-triazolo-[1,5-a]-pyrimidines as described in US-A 4,727,017, and other compounds such as benzenethiosulphonic acid, benzenethiosulphinic acid, benzenethiosulphonic acid amide. Other compounds that can be used as fog-inhibiting compounds are metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chapitre VI.

The fog-inhibiting agents or stabilizers can be added to the silver halide emulsion prior to, during, or after the chemical ripening thereof and mixtures of two or more of these compounds can be used.

The light-sensitive material of this invention may contain in the hydrophilic layer thereof a water-soluble dye as a filter dye, antiirradiation dye or antihalation dye or for various other purposes. Examples of such dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. The dye may be mordanted by a cationic polymer or the like. A description of such dyes is given in "Absorbing and Filter Dyes", Research Disclosure vol. 176, p. 23-26.

The silver halide emulsions prepared in accordance with the present invention can be used to form one or more silver halide emulsion layers coated on a support to form a photographic silver halide element according to well known techniques.

The photographic element of the present invention may 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. All kinds of fluorine-containing surface active agents may be used. 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.

Prior to coating any thickening agent may be used so as to regulate the viscosity of the coating solution, provided that they do not particularly affect the photographic characteristics of the silver halide light-sensitive photographic material. Preferred thickening agents include aqueous polymers such as polystyrene sulphonic acid, dextran, sulphuric acid esters, polysaccharides, polymers having a sulphonic acid group, a carboxylic acid group or a phosphoric acid group. Especially preferred for applications according to the present invention are colloidal silicas. Polymeric thickeners well-known from the literature resulting in thickening of the coating solution may be used independently or in combination, even with colloidal silicas. Amounts of it may be suitably selected according to the kinds of silver halide and the kinds of layers or compounds to which these thickening agents are to be added. Patents concerning thickening agents are U.S. Patent No. 3,167,410, Belgian Patent No. 558.143 and JP OPI Nos. 53-18687 and 58-36768. Negative effects on physical stability possibly resulting from the addition of polymeric compounds can be avoided by exclusion of those compounds and restricting extra additions to colloidal silica. The emulsions prepared and coated in accordance with the present invention are particularly advantageous for the formation of very thin emulsion layers, e.g. layers from 0.5 to 1.5  $\mu\text{m}$  thickness. Such thin coated layers offer besides the rapid processing applicability and the rapid drying of the wet processed material an improvement in sharpness.

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, and plasticizers as described below.

The gelatin binder of the photographic element, 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, chromium salts e.g. chromium acetate and chromium alum, aldehydes e.g. formaldehyde, glyoxal, and glutaraldehyde, N-methylol compounds e.g. dimethylolurea and methyloldimethylhydantoin, dioxan derivatives e.g. 2,3-dihydroxy-dioxan, active vinyl compounds e.g. 1,3,5-triacryloyl-hexahydro-s-triazine, active halogen compounds e.g. 2,4-dichloro-6-hydroxy-s-triazine, and mucohalogenic acids e.g. mucochloric acid and mucophenoxychloric acid. These hardeners can be used alone or in combination. The gelatin binder can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts.

The emulsion may be coated on any suitable substrate such as, preferably, a thermoplastic resin e.g. polyethyleneterephthalate or a polyethylene coated paper support.

If apart from the silica sol (an) additional protective colloid(s) is (are) present during the precipitation, then suitable additives for improving the dimensional stability of the photographic element may be added, 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, sulfoalkyl (meth)acrylates, and styrene sulphonic acids.

Plasticizers suitable for incorporation in the emulsions according to the present invention are e.g. glycol, glycerine, or the latexes of neutral film forming polymers including polyvinylacetate, acrylates and methacrylates of lower alkanols, e.g. polyethylacrylate and polybutylmethacrylate.

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.

Spacing agents, the average particle size of which is comprised between 0.2  $\mu\text{m}$  and 10  $\mu\text{m}$  can also be used. 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 silver halide emulsions can be used in various types of photographic elements such as i.a. in photographic elements for graphic arts and for so-called amateur and professional photography, diffusion transfer reversal photographic elements, low-speed and high-speed photographic elements, X-ray materials, etc.. In a preferred embodiment the photographic silver halide emulsions are used in X-ray materials.

The following examples illustrate the invention. All percentages are percentages by weight unless otherwise stated.

## EXAMPLES

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### Example 1

A photographic silver iodobromide emulsion containing 2.0 mole % of silver iodide was prepared by the single jet method in a vessel containing 75 ml of 15 % silica sol 'Kieselcol 500' (trademarked product of  
10 Bayer AG), 2.5 g of 3,6-dithio-1,8-octanediol as a grain growth accelerator and 50 ml of a 1 % stabilizing sulfonium compound of the type described in EP 0392092. The temperature was stabilized at 55 °C. The obtained emulsion was of an average grain size of 0.50  $\mu\text{m}$ , containing approximately 60 g of silver nitrate per kg of the dispersion after addition of 3 moles of silver nitrate at a constant rate of 150 ml.min<sup>-1</sup>.

After physical ripening the original pH value of 4.8 was adjusted to a value between 2.5 and 3.0 with  
15 hydrochloric acid.

After 15 minutes about  $1.0 \cdot 10^{-3}$  mole of gelatin (M.W. +/- 10.000) pro 100 g of silica was added to the dispersion. Stirring was ended after addition of this flocculating agent.

The emulsion was coagulated and after sedimentation the supernatant liquid was removed by means of a siphon.

20 Hereafter a scrape-rudder was placed and the sandy-structured, qualitatively well treatable flocculate was washed after adding 4 l of cool demineralised water. It is important to note that it is necessary to readjust the pH value at about 2.5 to 3.0 by slowly adding diluted sulphuric acid 1N. The washing procedure was repeated twice.

Redispersation was carried out after the addition of demineralized water, quickly stirring the flocculate  
25 during 15 minutes, rising the temperature to 45 °C and addition of gelatin to get an emulsion with a weight ratio of gelatin to silver nitrate of 0.28. The whole redispersation procedure took 60 minutes and before the emulsion was cooled pH was brought to a value of 6.5. The obtained silver halide crystal was of an average grain size diameter of 0.50  $\mu\text{m}$ , containing an amount of silver bromiodide emulsion corresponding to approximately 180 g of silver nitrate pro kg.

30 As a comparative emulsion with the same halide composition the silver halide crystals were prepared by a conventional single jet method in a vessel containing 40 g of ftaloyl gelatin. The ammoniacal silver nitrate solution was held at 42 °C as well as the emulsion vessel, containing the halide salts. At a constant rate of 300 ml per minute the precipitation time was ended after 10 minutes and followed by a physical ripening time of 40 minutes. After that time an additional amount of 20 g of gelatin was added. The obtained  
35 emulsion was of an average grain of 0.62  $\mu\text{m}$  and contained approximately 90 g of silver nitrate per kg of the dispersion after addition of 3 moles of silver nitrate.

After addition of sulphuric acid to a pH value of 3.5 stirring was stopped and after sedimentation the supernatant liquid was removed. The washing procedure was started after a scrape-rudder was installed and after addition of polystyrene sulphonic acid in the first turn to get a quantitative flocculate without silver  
40 losses.

During the redispersation of the emulsion 150 g of gelatin were added so that the weight ratio of gelatin to silver nitrate was 0.42, the emulsion containing an amount of silver bromiodide equivalent with 190 g of silver nitrate pro kg.

Both emulsions were chemically ripened with sulphur and gold at 47 °C for 4 hours to get an optimized  
45 relation between fog and sensitivity and were stabilized with 4-hydroxy-6-methyl-1,3,3a-tetrazaindene before coating on both sides of a polyester support of 175  $\mu\text{m}$  thickness. Amounts of coating solutions were the same in both cases in the emulsion layer as well as in the protective layer. Differences were in coating amounts of silver halide crystals, expressed as the equivalent amount of silver nitrate and of gelatin in the emulsion layer are:  $2 \times 4.41 \text{ g/m}^2$  for the comparative example and  $2 \times 3.34 \text{ g/m}^2$  for the silica emulsion, the  
50 amount of gelatin  $2 \times 1.05$  and  $2 \times 0.50 \text{ g/m}^2$  respectively, so that the ratios of gelatin to silver nitrate for both emulsions were approximately 0.24 (for the comparative example) and 0.15 (for the example corresponding to the invention) respectively.

The film was exposed to visible light coming from projection lamps (130V; 250W) for an exposure voltage of 90V during 0.1 s at a distance of 1.8 m from the film, through a continuously varying carbon-coated wedge(wedge constant 0.15), a densitometric filter with a density of 0.30 and a "Corning filter 5850"  
55 as a blue filter with a density 2.64 (measured with a Macbeth TR 924 densitometer). The radiographic materials were automatically processed, including the steps of processing (24 s at 34 °C), fixing (24 s at 34 °C), rinsing (24s at 20 °C) and drying (18s at 40 °C).

The developing bath used had a pH of 10.1 and comprised the following ingredients per litre

hydroquinone	120 g
1-phenyl-3-pyrazolidine-1-one	6 g
5-nitroindazole	1 g
methyl-6-benzotriazole	0.36 g

The following sensitometric data are listed in table 1:

- sensitivity(S), measured at a density of 1.0 above fog and expressed as log Ixt value
- gradation(GRAD), measured as an average gradient between densities of 0.25 and 2.00 above fog
- maximum density(DMAX)
- coverage power(CP), expressed as the maximum density per g AgNO<sub>3</sub> coated
- statical pressure sensibilization(SPS) (qualitatively evaluated at the site where the coating number was punched)
- dynamical pressure desensitization(DPDS) ( quantitatively expressed as the density-difference at D=1.50+fog for the reference sample, between this reference sample and a sample of the same coating material, being subjected to a dynamic folding procedure to be described as folding the material over an axle and transporting it over this axle. The axle has a central part where no pressure fog interferes, serving as a reference part. Immediately after this procedure the material is exposed for 0.0001 s with a Xenon-flash type EG&G FX272)
- darkroom light sensitivity(DRLS): density difference between exposed and unexposed part of the film, the exposed part being exposed to darkroom light during 3 minutes with a darkroom filter GBX3, so that the light intensity at the film is 36 lux.

TABLE 1

	S	GRAD	DMAX	CP	SPS	DPDS	DRLS
comparative example	1.00	2.88	4.13	47	comp,	-0.13	0.21
invention	1.00	2.83	3.46	52	better	-0.09	0.11

Obviously for the same sensitivity of both materials, the material according to the invention is better with respect to coverage power, statical pressure sensitization, dynamic pressure desensitization and darkroom light sensitivity.

It is also interesting to look at the experimental data in Table 2 after keeping the material for 24 hours at 57°C and 34% RH (relative humidity), followed by exposure and processing. In this table the wet scratch resistances measured for both sides of the material are also included (SR1 and SR2). For this experiment the layers were swelled in demineralized water of 20°C, whereupon the material was loaded with the continuously increasing pressure of a steel bullet while in the mean time moving the material relatively thereto. The value of the pressure was noted at the moment the material was scratched. The higher the value, the better the scratch resistance.

TABLE 2

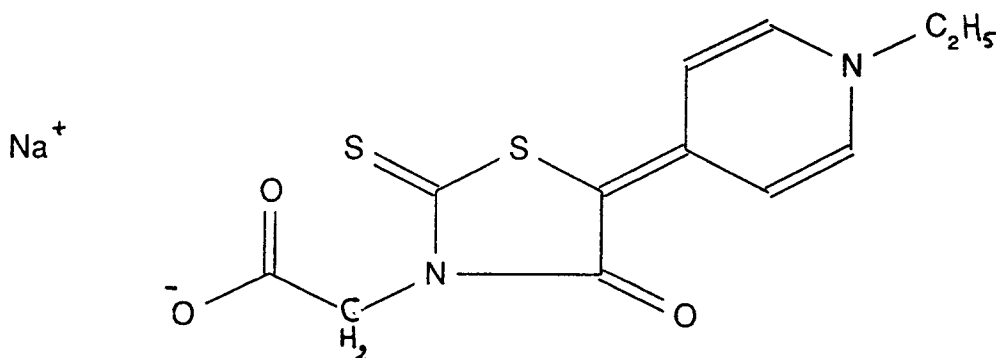
24 hours 57°C/34%R						
	S	GRAD	DMAX	CP	SR1	SR2
comparative example	1.02	2.68	3.84	43	190	170
invention	1.05	2.76	3.42	51	190	180

It is clear that the behaviour of the material according to the invention is better with reference to sensitivity, and coverage power. Also concerning scratch resistance no disadvantages are observed, although the gelatin content of the material according to the invention is considerably lower as mentioned above.



## Example 2

The same emulsions were prepared as in the first example, except for the fact that the emulsions were prepared at a 3°C higher temperature of the vessel and that the emulsion according to the invention was spectrally sensitized with a blue sensitizer according to the formula



which was added to the emulsion after redispersion of the flocculate, before chemical ripening in an amount of 0.6 mg per g  $\text{AgNO}_3$ .

The sizes of the silver halide crystals were 0.69 and 0.50  $\mu\text{m}$  respectively with an increase of the heterogeneity of both distributions with 15% versus the emulsions being precipitated at lower temperatures. Total amounts of the silver halide emulsions coated were 7.96  $\text{g/m}^2$  and 6.96  $\text{g/m}^2$  expressed as the equivalent amount of  $\text{AgNO}_3$  respectively for the comparative emulsion and for the emulsion according to the present invention. Total amounts of gelatin coated in the emulsion layer were 1.70 and 1.02  $\text{g/m}^2$ . The protective layer was the same as in the first example, as well as the polyester undercoat layer.

In Tables 3 and 4, an identical evaluation as in the previous tables 1 and 2 is given.

Table 3

	S	GRAD	DMAX	CP	SPS	DPDS	DRLS
comparative example	1.30	3.09	3.68	46	comp.	-0.17	0.66
invention	1.29	2.95	3.62	52	better	-0.15	0.50

For both materials with an equal but twice increased sensitivity versus the foregoing materials the same conclusion can be drawn as in the first example. After storing of the material, the conclusions formulated concerning the data in Table 2 are confirmed in Table 4.

Table 4

36 hours 57°C/34% RH						
	S	GRAD	DMAX	CP	SR1	SR2
comparative example	1.34	2.76	3.28	41	160	150
invention	1.38	2.87	3.50	50	160	180

Summarized we can say that the objectives of the invention can be realized with materials according to the present invention: a material is obtained that has better pressure characteristics and a comparative scratch resistance even when the emulsion layer is containing only one half of the gelatin of the emulsion layer with a "conventional" emulsion containing gelatin as a protective colloid in the precipitation. Besides the relationship between crystal size and sensitivity as well as the coverage power is remarkably advantageous for the material containing the "silica emulsion", allowing a lower coating amount of the silver halide. The thinner emulsion layer combined with the smaller coating amount of the silver halide makes the

material especially suitable for rapid processing purposes.

## Claims

- 5 1. Method of preparing a silver halide light-sensitive photographic material having a support and, provided thereon, at least one hydrophylic colloid layer including at least one light-sensitive silver halide emulsion layer characterised in that said light-sensitive silver halide emulsion layer is coated from an emulsion prepared by the steps of
  - 10 - precipitating silver halide in colloidal silica as a protective colloid in the absence of any polymeric compound(s) capable of forming hydrogen bridges with colloidal silica,
  - desalting the emulsion and redispersing the silver halide emulsion in the presence of gelatin,
  - chemically ripening the silver halide emulsion crystals,
  - 15 - finishing the emulsion ready for coating so that in said emulsion ready for coating the ratio of gelatin to silver halide expressed as silver nitrate is comprised between 0.05 and 0.40 and the ratio of silica to silver halide expressed as silver nitrate is comprised between 0.02 and 2.0.
2. Method of preparing a photographic material according to claim 1, wherein in the said silver halide emulsion layer the weight ratio of the amount of gelatin to the coated silver amount, expressed as the equivalent amount of silver nitrate, has a value between 0.15 and 0.30.
- 20 3. Method of preparing a photographic material according to claim 2, wherein in the said silver halide emulsion layer the weight ratio of the amount of silica to the coated silver amount, expressed as the equivalent amount of silver nitrate, has a value between 0.02 and 1.0.
- 25 4. Method of preparing a photographic material according to any of the preceding claims, wherein in the said light-sensitive silver halide emulsion layer the silver halide crystals are spectrally sensitized.
5. Method of preparing a photographic material according to any of the preceding claims, wherein in the said light-sensitive silver halide emulsion layer the silver halide emulsion crystals have been chemically ripened in the presence of a spectral sensitizer.
- 30 6. Method of preparing a photographic material according to claim 5, wherein the spectral sensitizer is a blue sensitizer.
- 35 7. Method of preparing a photographic material according to any of the preceding claims, wherein said material is a radiographic material.
8. Method of preparing a photographic material according to claim 7 wherein at least one hydrophylic emulsion layer is coated on at least one side of the support.



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## EUROPEAN SEARCH REPORT

Application Number

EP 92 20 2359

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)
D,A	EP-A-0 392 092 (AGFA-GEVAERT N.V.) * claims; page 9 example XVIII * ---	1-3	G03C1/04 G03C1/015 G03C5/16
A	US-A-4 001 022 (M.R.V.SAHYUN) * column 5, line 30 - line 38; claims * ---	1-3	
A	EP-A-0 391 405 (FUJI PHOTO FILM COMPANY) * page 74, line 36 - line 47; claims * ---	1-8	
A	EP-A-0 264 788 (KONISHIROKU PHOTO INDUSTRY CO.) * page 20, compounds (64), (65) * ---	4-8	
A	GB-A-2 085 180 (AGFA-GEVAERT AG) * page 9, line 1 - line 44; claims * ---	1	
A	FR-A-2 017 463 (AGFA-GEVAERT AG) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			G03C
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 26 NOVEMBER 1992	Examiner STOCK H.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	