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(54) Silver halide light-sensitive material with colloidal silica as protective colloid coated from layers without or with minimum amounts of gelatin as a binder material

(57) A light-sensitive silver halide photographic material is disclosed, said material comprising a support and one or more hydrophilic colloidal silver halide emulsion layers having silver halide crystals with colloidal silica as a protective colloid the said layer(s) having a gesi, defined as ratio by weight of gelatin binder to silver, in the range from 0 to less than 0.05 and a sisi, defined as ratio by weight of silica to silver, in the range from 0.01 to less than 0.10, wherein said weight of silver in the calculation of gesi and sisi is expressed as an equivalent amount of silver nitrate.

Description

1. Field of the invention.

The present invention relates to silver halide photographic materials coated from layers without or with minimum amounts of gelatin as a binder material.

2. 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 a stringent demand therefore for even more rapid processing.

The above-mentioned tendency is also present in the field of e.g. silver halide light-sensitive X-ray film materials as e.g. medical radiographic films. A 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 an 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 processed results ready for diagnosis.

Particularly in the midst of a surgical operation the viewing in no time of the finished radiographic image is a necessity!

In order to meet the above wishes in the medical field, it is desired 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 respect to reach an adequate sensitivity and image density, is to reduce the amount of swellable binder.

The most well-known binder particularly in photographic applications is gelatin. As has been established in EP-A 0 528 476, a solution has been found in order to reduce and/or to replace gelatin by providing silver halide emulsions the silver halide crystals of which have been prepared in colloidal silica and to provide a method of preparing a silver halide photographic material coated from said emulsions wherein a ratio of gelatin to silver halide expressed as an equivalent amount of silver nitrate is comprised between 0.05 and 0.40, preferably between 0.15 and 0.30, and a ratio of silica to silver halide expressed as an equivalent amount of silver nitrate is comprised between 0.01 and 2.0 and more preferably between 0.02 and 1.0.

However even with light-sensitive layers having such low gesi values, it was not yet possible to reach a preferred level of low swelling degrees as a result of water absorption in the processing of said materials. Especially the presence of higher amounts of gelatin coated as a binder in adjacent non-light-sensitive layers is not in favour of rapid drying properties in the preferred rapid processing cycles.

Moreover gelatin used as a binder in the layers of silver halide photographic materials is known as a medium absorbing ultra-violet rays, as has e.g. been described in US-P 5,284,744. This reduces sensitivity which may be disadvantageous in applications related with ultraviolet emitting intensifying screens. Furthermore gelatin is known to disturb doping procedures with (complex) metal ions in the preparation of silver halide crystals, which may lead to irreproducible sensitometric results, especially for different exposure times due to HIRF and/or LIRF defects as set forth in the same reference.

Physicochemical imperfections of gelatin are further well-known as e.g. brittleness at low degrees of relative humidity and sticking at high degrees of relative humidity of the environmental atmosphere. Moreover brittleness is a phenomenon which appears when ratio amounts of silica sol versus silver (sisi values) are enhanced, as e.g. in EP-A 0 392 092, where it has been established that for a ratio of silica versus silver halide coated of more than 0.5 no supplemental hardening of the coated layer is required, but where no suggestion is made of brittleness of the said layer. However when gesi values, expressing ratio amounts of gelatin to silver, are decreased the problem tends to become more and more severe.

From the viewpoint of ecology, there is in addition an ever lasting demand to 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 salt in the coated layers without coming into conflict with specific demands related with sensitometry and image quality so that new, more fundamental ways were explored.

3. Objects of the invention.

It is an object of the present invention to provide a silver halide light-sensitive photographic material coated, for ecological reasons, with low amounts of silver (halide) salt in its light-sensitive layer(s), in a binder medium containing minimum amounts of gelatin or being substantially free from gelatin, wherein said material has suitable sensitometric properties (fog, sensitivity, covering power) and physical properties such as e.g. high drying velocity in a rapid wet processing cycle wherein no haze, coagulation due to sludge formation and especially no brittleness is observed.

4. Summary of the invention.

In order to reach the objects of this invention a light-sensitive silver halide photographic material is disclosed, said material comprising a support and one or more hydrophilic colloidal silver halide emulsion layers having silver halide crystals with colloidal silica as a protective colloid the said layer(s) having a gesi, defined as ratio by weight of gelatin binder to silver, in the range from 0 to less than 0.05 and a sisi, defined as ratio by weight of silica to silver, in the range from 0.01 to less than 0.10, wherein said weight of silver in the calculation of gesi and sisi is expressed as an equivalent amount of silver nitrate.

5. Detailed description of the invention.

In this invention a starting point after precipitation of silver halide is a ratio of gelatin to silver, expressed as an equivalent amount of silver nitrate, of 0, which is adjusted after precipitation to a value of less than 0.05 by adding an adapted amount of gelatin at the stage of or after redispersing a desalted dispersion of silver halide emulsion crystals having colloidal silica as a sole protective colloid during precipitation. It is clear that, if necessary, no gelatin is added and that a gesi value having a value of 0 is maintained.

An essential protective colloid in this invention is silica, wherein the ratio of silica to silver halide salt, again expressed as an equivalent amount of silver nitrate, is determined at the stage of precipitation the said silver hlaide salt or, if performed so, after further addition of silica at the redispersion stage or later, thereby acting as a binder material. Said ratio, also called 'sisi' has a value from 0.01 to less than 0.10 in order to have satisfying physical properties according to the objects of this invention. The most remarkable difference between silver halide emulsions precipitated in colloidal silica and those prepared in gelatinous medium is the fact that colloidal silica is effectively locally surrounding the silver halide crystal, decreasing the adsorption of a competitive protective colloid like gelatin and protecting the said silver halide crystals effectively against pressure phenomena even for coated layers having very low values of gesi, as in the preferred range from 0 to less than 0.05 as claimed in this invention: as a ratio by weight of gelatin to silver halide decreases the effect is more pronounced due to the protective action of silica adsorbed at the surface of the precipitated silver halide. Such a material according to the present invention is clearly different from the material described e.g. in GB-A 1 276 894, wherein precipitation of silver halide crystals is performed effectively in the presence of a hydrophilic organic binder and wherein silicic acid, present in an amount of at least 50 % by weight, based on the total amount of binder in the finished silver halide emulsion layer is added after the washing step. This means that silicic acid is not added as a protective colloid in the preparation step of the silver halide crystals, but as a binder material only in the preparation step of the layers to be coated. The difference between a protective colloid and a binder material should be clearly understood: a protective colloid protects the silver halide crystals by surrounding them; a binder material is not in direct contact with the silver halide crystals but makes the layers containing the said protected crystals coatable.

In wet processing applications of silver halide photographic materials the presence of materials according to the present invention results in a weaker inhibition of the development, thus providing more rapid processing and this further results in the absence of sensitisation or desensitisation marks after processing.

In addition thereto in the said wet processing an increase of the covering power, defined as density obtained per weight unit of developed silver halide, can be realised. This effect is due to the formation of thin, homogeneously divided silver filaments generated during the rapid development process. As a result lower amounts of coated silver salt are required, offering the same maximum density as for comparative emulsions precipitated in gelatin.

The photographic silver halide for use in materials according to the present invention can be precipitated by mixing alkali halide and silver nitrate solutions in colloidal silica medium under partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide grains for use 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" as e.g. spectral sensitisers or stabilisers, may be very 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).

An average size of the silver halide grains used in accordance with the present invention may range from 0.01 to 7 μm, preferably from 0.3 to 3 μm. A size distribution of 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 in order 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 as 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 in the photographic emulsions of the materials 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 rhodium, iridium, ruthenium, cadmium, zinc and lead ions, commonly present as complex ions. There are no restrictions concerning the halide composition : chloride, bromide, iodide and any combination thereof may be used. Preferred are silver bromide, silver bromoiodide, silver chloride, silver chlorobromide, silver chloroiodide and silver chlorobromoiodide emulsions. Two or more different, separately formed silver halide emulsions may be mixed and used in coatings and materials 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. Said emulsions or nuclei can e.g. be added after generation "in situ" in a separate vessel located near the reaction vessel wherein emulsions according to this invention are precipitated.

Specific preparations with respect to crystal habit and/or halide composition of silver halide emulsions in colloidal silica have e.g. been described in EP-A's 0 677 773; 0 682 287; 0 649 051 and 0 754 964.

Well-known silica sols are suitable for use in the preparation method and material obtained according to the present invention. Suitable silica sols are commercially available such as the "Syton" silica sols (a trademarked product of Monsanto Inorganic Chemicals Div.), "Ludex" silica sols (a trademarked product of duPont de Nemours & Co., Inc.), "Nalco" and "Nalcoag" silica sols (trademarked products of Nalco Chemical Co) and "Kieselsol, Types 100, 200, 300, 500 and 600" (trademarked products of Bayer AG) without however being limited hereto.

Light-sensitive silver halide emulsion prepared for use in materials according to the present invention can be chemically sensitised 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 sensitisation can be carried out by effecting the ripening in the presence of small amounts of compounds containing sulphur, selenium and/or tellurium as e.g. thiosulphate, thiocyanate, thioureas, selenocyanate, selenosulphate, selenourea, phosphorselenide, the corresponding telluro-derivatives and further sulphites, mercapto compounds, and rhodanines. The emulsions can be sensitised by means of a combination of gold-sulphur, gold-selenium, gold-tellurium ripeners or combinations thereof as e.g. gold-sulphur-selenium, and further by means of reductors as e.g. tin compounds as described in GB-A 789,823, amines, hydrazine derivatives, formamidine-sulphinic acids, and silane compounds. When use is made of sulphur and/or selenium compounds the right choice thereof is predetermined by the lability of the compounds in the reaction medium during chemical sensitisation as this is determining the reaction kinetics thereof and the efficiency with which the said sensitisation has been performed in order to get an optimised fog-sensitivity relationship.

Chemical sensitisation can further be performed with small amounts of Ir, Rh, Ru, Pb, Cd, Hg, Tl, Pd, Pt, or Au. One of these chemical sensitisation methods or a combination thereof can be used. The chemical sensitisation is generally carried out under well-defined conditions of pH, pAg, temperature, gelatine, silver halide and sensitiser concentration until sensitivity and fogging are both optimal. Especially in the case of emulsion crystals with a high internal sensitivity, the surface should be optimally chemically sensitised because otherwise its sensitivity is not sufficient in a surface developer.

It is even possible to add 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, silver halide crystals are chemically sensitised in the presence of a spectral sensitiser, 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 sensitisation should start concurrently with chemical sensitisation, even entirely preceding chemical sensitisation as has been mentioned in Research Disclosure 22534, p. 28, including also alternative procedures such as introducing a portion of sensitising dye prior to chemical sensitisation and the remaining portion at the end, suggested e.g. by Locker et al, US-A 4,225,6,66. In a preferred embodiment a blue or a green sensitising dye is added before addition of chemical ripening agents and/or during chemical sensitisation. Spectral sensitisation can be improved by chemical sensitisation methods as has been described e.g. in US-A's Nos. 3,917,485 and 3,966,476 and in EP-A 0 712 034.

Chemically ripening in the presence of spectral sensitisers has further 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.

Silver halide photographic materials according to this invention thus preferably comprise spectrally sensitised silica silver halide crystals present in a hydrophilic light-sensitive coating composition wherein spectral sensitisation is performed by addition of at least one spectral sensitiser after precipitation of the said silica silver halide crystals but before redispersing the said crystals.

When spectral sensitisers are acting as site directors in the preparation of e.g. tabular silver halide emulsion grains it is preferred to add a part thereof during silver halide precipitation, more preferably during tabular growth, after nucleation.

A positive effect of addition of spectral sensitisers before and/or during chemical ripening is e.g. observed when gelatin-free silica emulsion crystals peptised with polyvinylalcohol or a derivative therefrom (e.g. modified polyvinylalcohol) are spectrally sensitised with a green sensitising oxacarbocyanine and/or imidacarbocyanine compound: addition of the said spectral sensitisers before addition of (modified) polyvinylacohol (commonly added after redispersion of silica silver salt crystals) shows J-aggregation, whereas addition of the same peptiser(s) before addition of the said green sensitising compound(s) doesn't show J-aggreagation tendency.

Besides spectral sensitisers, which act as sensitising aids, compounds as azaindenes, azapyridines or azapyrimidines, the latter compounds being well-known as stabilisers, reducing fog and increasing sensitivity of silver halide emulsions may alternatively be added before or after the addition of the chemical ripening agents and may even portionwise be added at different stages during the sensitising and/or coating preparation procedure.

Descriptions obtained therefrom can be found e.g. in US-A 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 this invention can be spectrally sensitised 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 sensitisation 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 sensitisation activity, or certain other compounds, which do not substantially absorb visible radiation, can have a supersensitising effect when they are incorporated together with said spectral sensitising agents into the emulsion. Suitable supersensitisers are i.a. heterocyclic mercapto compounds containing at least one electronegative substituent as described e.g. in US-A 3,457,078: nitrogen-containing heterocyclic ring-substituted amino-stilbene compounds as described e.g. in US-A 2,933,390 and in US-A 3,635,721; aromatic organic acid/formaldehyde condensation products as described e.g. in US-A 3,743,510; cadmium salts, and azaindene compounds.

To the silver halide emulsion prepared for use in materials in accordance with the present invention may be added compounds preventing the formation of fog or stabilising 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 stabiliser to the silver halide emulsion. Suitable examples are i.a. the heterocyclic nitrogen-containing compounds such as benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercapto-thiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles (preferably 5-methylbenzotriazole), nitrobenzotriazoles, mercaptotetrazoles, in particular 1-phenyl-5-mercapto-tetrazole and derivatives thereof having e.g. a carboxylic or another acid substituted group, 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-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 e.g. the compounds described in Research Disclosure N° 17643 (1978), Chaptre VI and RD N° 36544 (1994), Chaptre VII. Fog-inhibiting agents or stabilisers can be added to the silver halide emulsion prior to, during, or after the chemical ripening thereof as already suggested hereinbefore but also prior to coating. Mixtures of two or more of these compounds can be used.

The light-sensitive material of this invention may contain in one or more hydrophilic layers thereof a water-soluble dye as a filter dye, anti-irradiation 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 and RD 36544 (1994).

Silver halide emulsions prepared for use in materials 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 one or more photographic emulsion layer(s) or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides as 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, sensitisation, 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's 3,038,805; 4,038,075 and 4,292,400. Other useful development accelerators have been described in EP-A 'S 0 634 688 and 0 674 215.

Prior to coating any thickening agent may be used in order 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. Suitable examples thereof have been described in EP-A No. 96201653, filed June 13, 1996.

As is well-known problems related with low concentrations of gelatin permit the coating of thin layers. However none of the materials described in BE-Patent Applications 611 623 and 665 860; and in US-A's 3,063,838; 2,942,974; 3,085,009 and 3,338,716 has hitherto been entirely satisfactory as haze, coagulation due to sludge formation in the processing and brittleness were exhibited. Moreover increases in viscosity have been restrained by e.g. the pH of the particular emulsion medium. Improved methods for increasing the viscosity of dilute photographic emulsions have e.g. been described in RD 11012, disclosed June 1973. Preferred thickening agents include e.g. 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. For applications according to the present invention colloidal silicas are not a preferred choice with respect to thickening of hydophilic colloidal layers as they enhance the "sisi" value in the light-sensitive emulsion layer(s). Therefore better viscosity improving polymers are e.g. 2-acrylamido-2-methylpropane sulphonic acid-acrylamide copolymer for coating formulations consisting of copolymers from aliphatic sulfonic acid monomers with water-soluble nonionic monomers have e.g. been described in RD 23406, published October, 1983. Polymeric thickeners well-known from the literature resulting in thickening of the coating solution may be used independently or in combination. 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 should be added. Patents concerning thickening agents are further US-A 3,167,410; Belgian Patent No. 558.143 and JP-A's 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 as e.g. layers having a thickness from 0.5 to 5 μm and even more preferred from 0.5 to 1.5 μm. Such thin coated layers offer besides the rapid processing applicability and the rapid drying of the wet processed material an improvement in sharpness as has e.g. been described for rapid processable silver halide material containing reduced gelatin content with defined amounts in the emulsion layer (at least 1.0 g/m^2), the overcoat layer (at least 1.5 g/m^2) and in the material (total amount limited to 3.5 g/m^2) have been described in US-A 5,206,128.

In the absence of gelatin it has moreover been proved that coatings can be made of emulsions and dispersions in the presence of polymers and derivatives thereof as e.g. polyvinyl alcohol, polyacrylic acid, polyoxyalkylenes, polyethylene-imine, cellulose ethers and cellulose esters which are not compatible with gelatin. Another compound suitable for use in an improved layer which reduces haze in a photographic element is a cellulose derivative as has been described in US-A 3,561,967.

According to this invention a silver halide light-sensitive photographic material is provided wherein said at least one hydrophilic layer further comprises at least one of polymeric binders selected from the group consisting of poly-N-vinylpyrrolidone, dextranes, cellulose compounds and derivatives thereof and copolymers of vinylidene chloride-methacrylate-itaconic acid or methyl(meth)acrylate-butadiene-itaconic acid. Poly-N-vinylpyrrolidone e.g. has a wide solubility and compatibility range, complexing and detoxifying ability, physiological acceptibility, protective-colloid action, film-forming ability and adhesive quality. As an example of cellulose derivatives there is referred to hydroxyethylcellulose which forms films with good clarity and moderate strength. Cross-linking of the polymer chains therein is usually performed by reaction of a polyfunctional compound with the available hydroxyl groups in the polymer as e.g. by reaction with dialdehydes as e.g. glyoxal, glutaraldehyd, 2-hydroxyadipaldehyde or by reaction with dimethylolurea and water-soluble urea- and melamine-formaldehyde resins.

In the presence of small amounts of gelatin incorporation of stability enhancing polymers like polyacrylates, polymethacrylates and polyacrylonitiles or polyacrylic acids may be useful as has been described in EP-A 0 375 159. Improvements of elasticity properties of such layers can be attained by addition of styrene-butadiene latex compounds as has been described in US-A 3,359,108.

It is important to prepare coating solutions for e.g. subbing layers and protective overcoat layers that are compatible with the composition of the hydrophilic light-sensitive emulsion layers in the material according to this invention. Moreover good adhesion of the different layers with each other and with the support is required. Therefore subbing layers for film supports comprising a mixture of vinylidene chloride/alkyl acrylate or methacrylate/itaconic acid copolymer and a homopolymer of an alkyl acrylate or methacrylate as has been described in US-A 3,460,944 can be used. One or more subbing layer(s) comprising polyethylene acrylate ester as has been described in US-A 3,443,950 can also be very useful. Moreover improved adhesion for one or more subbing layer(s) comprising the said polymeric ester has been described in US-A 3,143,421. A method for the preparation of a polymeric subbing layer to enhance the adhesion between layers has further been described in US-A 2,698,235. Hydrophilic overcoat layers comprising vinylidene chloride-methylacrylate-itaconic acid copolymer, providing good adhesion to hydrophilic emulsion layers have been described e.g. in EP-A 0 395 164 and are recommended also for use in the material of this invention.

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 plasticisers as described e.g. in RD 36544 (1994).

The gelatin binder of the photographic element, if present, can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulphone type e.g. 1,3-vinylsulphonyl-2-propanol, bis-vinyl sulphonyl methane, better water-soluble hydroxy-substituted vinyl sulphonyl hardeners, chromium salts as e.g. chromium acetate and chromium alum, aldehydes as 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, if present, can also be hardened with fast-reacting hardeners such as carbamoylpyridinium salts. In the complete absence of gelatin use can be made of phosphoric acid and derivatives thereof in order to harden non-gelatinous binders as e.g. poly-N-vinylpyrrolidone.

The emulsion may be coated on any suitable substrate such as, preferably, a thermoplastic resin as e.g. polyethyleneterephthalate, polyethylenenaphthalate or a polyethylene coated paper support. If apart from 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, α-β-unsaturated dicarboxylic acids, hydroxyalkyl (meth)acrylates, sulphoalkyl (meth)acrylates, and styrene sulphonic acids.

Plasticisers 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 as 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's 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 μm and 10 μm can also be used. Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in a 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.

Methods of manufacturing a silver halide photographic material according to the present invention by coating hydrophilic layers thereof on at least one side of a support by slide-hopper, curtain-coating or doctor blade coating techniques followed by drying are preferred. The said coating techniques are described e.g. in RD 36544, september 1994. Slide-hopper coating techniques have been described e.g. in EP-A 0 383 347 and in DD-A 0 281 268; curtain coating techniques have e.g. been described in EP-A's 0 489 978 and 0 440 279 and in CS 195 403, wherein defects in multilayer photographic materials are eliminated by addition of acrylamide polymer or its copolymer with acrylic or methacrylic acid, acetonitrile or N-dialkylaminoalkyl acrylate. Improved coating of photographic compositions, allowing broader coating latitude by avoiding coagulation, have been described e.g. in US-A 5,268,263, wherein fluorinated polyalkylene imines and sulphonated surfactants are mentioned.

As a consequence in accordance with the present invention it has been shown that non-gelatinous or gelatin-poor hydrophilic layers can be coated with especially preferred characteristics as e.g. a low swelling degree (low water absorption) in favour of rapid drying properties in the (rapid) processing cycle, less ultraviolet absorption (as has e.g. also been suggested in US-A 5,284,744 wherein the specific use of potatoe starch as a binder for silver halide crystals has been disclosed), higher covering power and less pressure sensitivity and the absence of brittleness.

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..

Moreover heat-sensitive recording materials and more preferably photothermographic materials comprising an organic silver salt (commonly silver behenate) besides silver halide emulsion crystals precipitated in colloidal silica as a sole protective colloid are advantageously manufactured, as in this application very low amounts of gelatin are required and still more preferably in the case when gelatin should completely be avoided.

In a preferred embodiment the light-sensitive silver halide photographic material according to this invention is a silver halide photographic X-ray material, used for medical diagnostic purposes. The said X-ray material can be a single coated or double coated (duplitized) material for use in contact with one or more intensifying screen(s) containing luminescent phosphors. Said duplitized materials can have a symmetrical or an asymmetrical construction and contact can be made with two identical or two screens differing from each other in order to get specified speed-gradation-cross-over characteristics, depending on the specific diagnostic application wherein the said material is used.

Further preferred silver halide materials are laser recording materials used in laser imaging applications as has e.g. been described in EP-A 0 610 609 and EP-Application No. 96200622, filed March 7, 1996 or in graphic applications wherein lower amounts of silver coated are highly preferred.

The following examples illustrate the invention without however being limited thereto.

EXAMPLES

Example 1

A photographic silver iodobromide emulsion containing 2.0 mole % of silver iodide was prepared by the double jet method at a constant pAg value in a vessel containing 4000 ml of demineralised water and 300 ml of 15 % silica sol 'Kieselsol 500' (trademarked product of Bayer AG), 2.5 g of 3,6-dithio-1,8-octanediol as a grain growth accelerator and 50 ml of a 1 % stabilising sulfonium compound according to formula (I) given in Example I from EP-A 0 392 092.

The temperature was stabilised at 70°C. The precipitation stage was divided into two parts: 1.1 % of the silver nitrate was consumed in the nucleation step at a constant pAg (vs. Ag/AgCl as a reference electrode) of -45.6 mV and at a constant flow rate of 66.0 ml/min. of the silver nitrate and potassium bromide/iodide solutions; 98.9 % was consumed during the growth step, which proceeded at the same constant flow rate.

The emulsion obtained had an octahedrical habit and was of an average grain size of 0.50 μm, containing an amount of silver halide corresponding to approximately 60 g of silver nitrate per kg of the dispersion after addition of 3 moles of silver nitrate.

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

From this dispersion 200 ml were taken and 2-hydroxyethylether hydroxyethylcellulose (2% NATROSOL 250L) was slowly added as a flocculating agent in an amount of 11 ml after 15 minutes.

Stirring was ended after the end of addition of this flocculating agent and the emulsion coagulated. After decantation of the water containing soluble salts remaining after the precipitation stage, the coagulated emulsion was further washed twice.

The coagulated silica emulsion thus obtained was redispersed very easily after pH adjustment to a value of 6.5 and by addition per 500 g of the equivalent amount of silver nitrate of the following ingredients :

Polyvinylpyrrolidone (LUVISKOL K90: MW:700000; product from BASF)	15g
2-hydroxyethylether hydroxyethylcellulose (NATROSOL 250L; product from HERCULES/AQUALON BELGIUM NV)	50g
co(vinylidene chloride-methylacrylate-itaconic acid:86-09-10)	150 ml

After chemical sensitisation with optimum amounts of sulphur and gold a handcoating of the gelatin-free emulsion having a sisi of 0.09 thus obtained was made on polyethylene paper, said coating being called No. 1A.
No gelatin was added in the whole precipitation and flocculation procedure in order to prepare gelatin-free coatings.
The following emulsion coatings were made in an analogous way:

- Coating No. 1B: same as No. 1A, except for the use of 300 ml of copolymer (double amount versus in 1A).
- Coating No. 1C: same as No. 1B, except for omitting addition of NATROSOL 250L.
- Coating No. 1D: same as No. 1B, except for the addition of 5 g of 2-acrylamido-2-methyl propane sulphonic acid - acrylamide copolymer instead of NATROSOL 250L.
- Coating No. 1E: addition after coagulation and washing of 125 g of gelatin in order to get an emulsion having a gesi of 0.4.

Said coatings were fully developed at a temperature of 20°C after ca. 5 seconds in the classical G138 developer (trade name product from Agfa-Gevaert) and fixed within ca, the same short time. To illustrate the gain in covering power said coatings Nos. 1A-1E were developed at 20°C in developer G201 during 118 seconds, followed by fixation at the same temperature in fixer G334 during 118 seconds, both G201 and G334 being trademarked processing compositions from Agfa-Gevaert.

In Table 1 results are given from maximum densities Dmax, measured in transmission (TR) and in reflection (RFL) (under an angle of 45°), amounts of silver per square metre and covering power (in transmission: CP-TR; and in reflection: CP-RFL).
Sensitometric results were about equal for all coatings Nos. 1A-1E. Thanks to the low sisi value of the coatings, said coatings showed no brittleness.

Table 1

Coating No.	Dmax (TR)	Dmax (RFL)	Ag/m^2	CP-TR	CP-RFL
1A (inv.)	5.20	1.30	8.26	63.8	15.7
1B (inv.)	4.90	1.38	8.26	59.2	16.7
1C (inv.)	5.20	1.29	5.76	90.6	22.4
1D (inv.)	5.40	1.30	6.66	80.9	19.5
1E (comp.)	5.30	1.50	9.70	54.0	15.6

Especially coatings 1C and 1D are giving unexpectedly good results with respect to maximum density and covering power for such low amounts of silver coated: covering power increased with about 50 % for a silver coverage which was decreased with at least 30 % (from more than 8 to less than 6 g/m^2) as illustrated for the samples 1C and 1D if compared with the gelatinous coating 1E.

Example 2

The same emulsions were prepared as in Example 1, except for the fact that the emulsions were coagulated in the presence of 16 g of phthaloyl gelatin per 500 g of silver bromoiodide, expressed as an equivalent amount of silver nitrate. After decantation of the water containing soluble salts remaining after the precipitation stage, the coagulated emulsion was further washed twice.
The coagulated silica emulsion thus obtained was redispersed very easily after adjustment of the pH to a value of 6.5 by addition per 500 g of the equivalent amount of silver nitrate of the following ingredients :

Poly-N-vinylpyrrolidone (LUVISKOL K90: MW:700000)	30 g
LEXYL (20 % wt)	200 ml
KIESELSOL 500 (15 % wt)	300 ml
POLYDEXTRAN (M.W.10000: dextran/dextranphenylcarbonate: 5/1)	100 ml

After chemical sensitisation with optimum amounts of sulphur and gold a handcoating of the gelatin-free emulsion thus obtained was made on polyethylene paper, said coating being called No. 2A.

Coating No. 2B: same coating as No 2A, except for omitting POLYDEXTRAN.

Coating No. 2C (comparative coating): addition after coagulation and washing of 109 g of gelatin in order to get an emulsion having a gesi of 0.4.

Said coatings were again fully developed at a temperature of 20°C after ca. 5 seconds in the classical G138 developer (trade name product from Agfa-Gevaert) and fixed within ca. the same short time.

In order to illustrate the gain in covering power said coatings Nos. 2A-2C were developed at 20°C in developer G201 during 118 seconds, followed by fixation at 20°C in fixer G334 during 118 seconds, both G201 and G334 being trademarked processing compositions from Agfa-Gevaert. In Table 2 results are given from maximum densities Dmax, measured in transmission (TR) and in reflection (RFL) (under an angle of 45°), amounts of silver per square metre and covering power (in transmission: CP-TR: in reflection: CP-RFL), as in Example 1.
Sensitometric results were about equal for all coatings Nos. 2A-2C.

Table 2

Coating No.	Dmax (TR)	Dmax (RFL)	Ag/m^2	CP-TR	CP-RFL
2A (inv.)	5.23	1.28	7.01	74.81	18.26
2B (inv.)	5.55	1.34	7.11	78.06	18.85
2C (comp.)	4.99	1.28	7.58	65.83	16.89

To summarise: the objectives of this invention are realised with materials coated from photographic light-sensitive layers comprising silver halide emulsions precipitated in colloidal silica used as a protective colloid in conditions wherein said layers having a gesi from 0 to less than 0.05, for values of "sisi" of less than 0.1 as has been shown in the Examples.

Light-sensitive layers making part of said materials containing ingredients as shown in the Examples hereinbefore thus provide suitable photographic properties (fog, sensitivity, covering power) and the required physical properties (high drying velocity, absence of brittleness).

Claims

1. Light-sensitive silver halide photographic material comprising a support and one or more hydrophilic colloidal silver halide emulsion layers having silver halide crystals with colloidal silica as a protective colloid the said layer(s) having a gesi, defined as ratio by weight of gelatin binder to silver, in the range from 0 to less than 0.05 and a sisi, defined as ratio by weight of silica to silver, in the range from 0.01 to less than 0.10, wherein said weight of silver in the calculation of gesi and sisi is expressed as an equivalent amount of silver nitrate.

2. Material according to claim 1, wherein said hydrophilic colloidal layer further comprises a polymeric binder selected from the group consisting of poly-N-vinylpyrrolidone, dextranes, cellulose compounds and derivatives thereof and copolymers of vinylidene chloride-methylacrylate-itaconic acid or methyl(meth)acrylate-butadiene-itaconic acid.

3. Material according to claim 1 or 2, wherein said material is a silver halide photographic X-ray material.

4. Material according to claim 1 or 2, wherein said material is a laser recording material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 2778

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.6)
D,Y	EP 0 528 476 A (AGFA GEVAERT NV) 24 February 1993 * page 2, line 45 - page 3, line 37 *	1-4	G03C1/04 G03C5/16
Y	GB 1 276 894 A (AGFA-GEVAERT AG) 7 June 1972 * page 1, line 68 - page 2, line 10 *	1-4	
A	EP 0 517 961 A (AGFA GEVAERT NV) 16 December 1992 * page 3, line 12 - line 24; claims 1-4; example 1 *	1-4	
A	EP 0 670 517 A (KONISHIROKU PHOTO IND) 6 September 1995 * page 5, line 1 - line 3 * * page 5, line 32 - line 38; claim 5 *	1-4	
A	US 3 637 391 A (SALECK WILHELM ET AL) 25 January 1972 * column 2, line 69 - line 75 *	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	US 4 001 022 A (SAHYUN MELVILLE R V) 4 January 1977 * claims 1-5 *	1-4	G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 December 1997	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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