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(54) Method of preparing light-sensitive silver halide emulsions.

(57) This method comprises the coagulation, washing and redispersing procedure of a light-sensitive silver halide emulsion after precipitating silver halide in the presence of colloidal silica serving as protective colloid. From 10 to 40 % of gelatin with repect to silica are used as flocculating agent.

This invention relates to methods of coagulating, washing and redispersing light-sensitive silver halide emulsions, the silver halide of which has been precipitated in a colloid medium of silica and to photographic materials incorporating layers of such emulsions.

Light-sensitive silver halide emulsions are conventionally prepared by reacting an aqueous silver salt solution, e.g. silver nitrate, with an aqueous alkali metal halide solution to cause precipitation of silver halide in the presence of a protective colloid. After physical ripening to the desired average grain size and washing, a further amount of protective colloid may be added so that the emulsion may be subjected to chemical ripening.

The most commonly used protective colloid is gelatin which is a thermoreversible polymer, showing a sufficient gel strength after coating. Although possessing many advantages, the conventional gelatino-silver halide emulsion layers undergo considerable swelling and subsequent shrinkage upon absorption and release of processing liquids during image processing. This lack of dimensional stability under processing conditions can adversely affect image quality.

Especially the effect of gelatin, being adsorbed on and surrounding the silver halide crystal is fundamentally disadvantageous with respect to development characteristics, e.g. the spatial distribution of silver filaments and the related coverage power. Differences in photographic properties obtained between dry and wet coatings may be explained in this context.

Moreover, due to their rather slow absorption and release of the processing liquids, conventional gelatino-silver halide layers cannot meet the extremely rapid processing criteria which are often demanded.

With a view to forming light-sensitive layers which have good water-permeability but which have greater dimensional stability than the conventional gelatino-silver halide layers under processing conditions, many types of ingredients have been proposed for use instead of or in addition to gelatin. These proposed ingredients include various natural film-forming substances and synthetic resins, e.g. polyoxyethylene glycols, polyvinylpyrrolidone, starch and starch derivatives. For the most part these prior art binding agents have one or another disadvantageous effect on the mechanical or photographic properties of the light-sensitive layer. In particular they tend to reduce light-sensitivity.

Another substance proposed in the prior art as protective colloid binder in silver-halide emulsions is colloidal silica. This colloid has no or less adverse effects on light-sensitivity and as disclosed in UK Patent 1276894 silver halide emulsions comprising gelatin together with various proportions of silica sol as a binder have less tendency to swell on treatment with aqeuous processing liquids than conventional gelatino-silver halide emulsion layers of the same thickness.

However the necessity to restrict the concentration of the silica sol, for reasons of physical stability, limits the advantage which can be derived from the use of the sol in terms of for instance improved dimensional stability of photographic layers formed from the emulsion.

It has been disclosed in EP 0392092 to increase the amount of silica sol used as a protective colloid in the preparation of silver halide emulsions, without resulting in unacceptable physical instability of the emulsion.

According to that disclosure there is provided a method of preparing a light-sensitive silver halide emulsion by precipitating silver halide in the presence of colloidal silica serving as protective colloid, characterized in that the precipitation takes place in the presence of an onium compound having an emulsion-stabilising effect.

After precipitation, the emulsion has to be coagulated and washed. Coagulation in gelatineous medium can e.g. be effected by an alcohol or a salt or if the emulsion contains a sufficient amount of acid-coagulable gelatin derivatives or hydrogen bridge forming anionic polymeric compounds by addition of an acid to lower the pH value to the isoelectric point. Well-known examples of hydrogen bridge forming anionic polymeric compounds are polystyrene sulphonic acid and sulphonated copolymers of styrene, which are commonly used. Acid coagulable gelatin derivatives as phtaloyl or N-phenyl carbamoyl gelatin can be used, requiring only adjustment of the pH to the right value to cause the emulsion to coagulate.

Coagulation techniques have been described e.g. in U.S. Patent Specifications 2,614,928; 2,614,929 and 2,728,662.

Unfortunately these common techniques cannot be applied to silver halide emulsions the silver halide of which has been precipitated in silica medium. In these circumstances of concentration, temperature and pH, it is impossible to get a necessary clear supernatant liquid : the turbidity of it gives rise to unacceptable silver losses by decantation. Further washing procedures do even have no sense in the case of non-quantitive coagulation.

Alternative methods of coagulation for the silver halide emulsions prepared in silica have been described in EP 0392092 and include the desalting techniques by high-speed centrifuge, by dialysis and by ultrafiltration. These techniques are not only technically complex but it has moreover been found experimentally that a hardly removable deposit of silica is formed on the membranes, shortening the lifetime thereof.

It is an object of the present invention to provide a relatively simple but efficient coagulation technique for silver halide, precipitated in silica medium offering quite a lot of remarkable advantages, not only in the desalting step, but also in the redispersed stage and the subsequent stages of making the emulsion ready for coating.

According to the present invention there is provided a method of preparing a light-sensitive silver halide emulsion comprising the steps of precipitating the silver halide in the presence of colloidal silica serving as a protective colloid, coagulation washing the formed precipitate and redispersing the silver halide, characterised in that the coagulation proceeds in the presence of hydrogen-bridge forming polymer compounds, in amounts sufficient to form coagulable aggregates with silica particles.

From a range of experiments it has been found that a variety of hydrogen bridge forming polymers can be used as a flocculating agent, e.g. gelatin. polyethylene oxyde, polyethylene imide, polyacrylic acid, polyacetic acid, polyvinylalcohol, etc. and a combination of two or more of these agents. In a preferred embodiment gelatin is used as flocculating agent.

The quantity of flocculating agent can be optimized for each particular case. The amount should not be such that redispersion occurs.

Amounts of e.g. 1 to 40%, preferably 10 to 40% by weight of flocculating agent versus silica sol generally give rise to qualitatively good flocculates, which are transportable in a handsome way through e.g. conduct-pipes as they have a "sandy" structure, never showing sticking phenomena. The amount of silica normally used at the stage of precipitation is comprised between 2 and 20 parts by weight with respect to 100 parts by weight of silver nitrate used. This procedure is offering quite a lot of advantages e.g. it is even possible to produce powdery silver halide crystals by dry-freezing of this sandy flocculate.

On the other hand higher amounts of e.g. more than 40% by weight generally cause redispersion so that the desalting process is made impossible.

According to the present invention silver halide emulsions are prepared by the following steps :

a. Precipitating silver halide in aqueous silica medium having a pH above 4, the silica being preferably the sole protective colloid present.
b. Adjusting the pH of the silver halide emulsion to a value of 1.0 to 4.0, preferably from 2.5 to 3.
c. Adding to the emulsion vessel a hydrogen bridge forming polymer as flocculating agent.
d. Permitting the formation of aggregates after hydrogen-bridge formation.
e. Removing the clear supernatant liquid e.g. by means of a siphon or by decanting it.
f. Washing the flocculate e.g. the flocculate is stirred with a scrape-rudder rotating at a moderate velocity while or after the washing water is added to avoid the destruction of the well-formed sandy-structured flocculate, preventing the weak hydrogen-bridges from breaking.
g. Readjusting the pH to a value of 1.0 to 4.0, preferably from 2.5 to 3.0.
h. Removing the clear supernatant liquid.
i. Repeating procedure f to h if necessary to meet the desirable pAg-value demands.
j. Causing redispersion of the flocculate by adding an excess of a protective colloid or hydrogen-bridge forming polymer and stirring the flocculate with an increasing velocity.

The choice of protective colloid at the stage of redispersion is determined by further treatment conditions as e.g. chemical ripening, spectral sensitization, stabilization and preparation to coating.

It is quite obvious that the whole procedure may take place at higher or lower temperatures. To save time, it is not necessary to cool the dispersion at the end of the precipitation.

In order to redisperse the flocculate an excess of the original flocculating agents can be used in whatever an amount, which depends on the coating requirements. However other colloids than the hydrogen bridge forming polymers mentioned as flocculating agent, can be used in redispersing the coagulate.

As no gelatin is used as a protective colloid at the stage of precipitation of the silver halide in the presence of silica the temperature of the reaction vessel can be lowered without risking a jelly structure and unprotected silver halide crystals.

In a preferred mode of the invention, silica sol may be added at the stage of redispersion and the ratio by weight of silica sol over silver halide can be regulated. So in EP 0392092 even a value exceeding 1.0 is described to be the most preferable one if one wants to avoid the addition of supplemental hardening agents to the emulsion before or during the coating procedure. Any combination of ingredients, being compatible to form a stable colloid system before and during coating, may be used.

As the starting point after precipitation is a gelatin to silver nitrate ratio of zero, the ratio by weight of gelatin over silver nitrate can be adjusted by adding an adapted amount of gelatin. silica and/or suitable polymers at the stage of or after redispersing the coagulation washed emulsion. Even coating without gelatin is possible, especially on a paper undercoat or substrate.

The average size of the silver halide grains may range from 0.01 to 7 μm.

The size distribution of the silver halide particles of the photographic emulsions prepared according to the present invention 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.

According to the present invention the photographic silver halide can be precipitated by mixing the halide and silver solutions in the 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.

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 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 Rh^{3+}, Ir^{4+}, Cd^{2+}, Zn^{2+}, Pb^{2+}. There are no restrictions concerning the halide composition : chloride, bromide, iodide and any combination may be used.

Separately formed two or more different silver halide emulsions may be mixed for use 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 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 in accordance with the present invention is, after redispersion, a so-called primitive emulsion. However, 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. A mixture can also be made of two or more separately precipitated emulsions being chemically sensitized before mixing them.

The light-sensitive silver halide emulsions can be spectrally sensitized with methine dyes such as those described by F.M. Hamer in "The Cyanine Dyes and Related Compounds", 1964, John Wiley & Sons. Dyes that can be used for the purpose of spectral sensitization include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, 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 e.g. in US-A 3,457,078, nitrogen-containing heterocyclic ring-substituted aminostilbene compounds as described e.g. in US-A 2,933,390 and 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 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-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 metal salts such as e.g. mercury or cadmium salts and the compounds described in Research Disclosure N° 17643 (1978), Chaptre 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 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. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g higher contrast, sensitization, and development acceleration.

Development acceleration can be accomplished with the aid of various compounds, preferably polyalkylene derivatives having a molecular weight of at least 400 such as those described in e.g. US-A 3,038,805 - 4,038,075 - 4,292,400.

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

The binders of the photographic element, especially when the binder used is gelatin. can be hardened with appropriate hardening agents such as those of the epoxide type, those of the ethylenimine type, those of the vinylsulfone type e.g. 1,3-vinylsulphonyl-2-propanol, 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 binders 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.

polyethyelenterephtalate or a polyethylene coated paper support.

If, however, apart from the silica sol (an) additional protective colloid(s) is (are) present during the precipitation or added during or after redispersion, 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, sulphoalkyl (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.

In general, the average particle size of spacing agents is comprised between 0.2 um and 10 um. 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..

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

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 '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 % stabilizing sulfonium compound. The temperature was stabilized at 55°C. The obtained emulsion was of an average grain size of 0.50 µm, 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-1.

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

After 15 minutes about 10 g of gelatin (M.W. +/- 10.000) pro 100 g of silica sol 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.

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 too quickly stirring deteriorates the formed structure and 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.

EXAMPLE 2 (comparative example I)

A photographic emulsion was prepared according to the procedure described in Example 1; however no flocculating agent was added.

EXAMPLES 3 TO 12

Photographic emulsions were prepared according to the procedure described in Example 1, except that the following compounds were used as flocculating agents.

EXAMPLE 3

Gelatin in an amount as in example 1 was replaced by another inert type of gelatin, the viscosity being lower in this case (19.4 mPas instead of 32.8 mPas for a 10% solution at 40°C, measured with a Haake Rotavisco RV2 apparatus).

EXAMPLE 4

Same type of gelatin as in example 3, but in a higher amount, giving rise to a ratio by weight of gelatin to silver nitrate of 0.15, approximating a common value for precipitations in gelatineous medium at the end of the precipitation.

EXAMPLE 5

Instead of gelatin per 100 g of silica 6.6 g of polyethyleneimine ("Montrek 600", trademarked product from Dow Chemical), having recurring units corresponding to the formula

$(\text{-CH}_2\text{-CH}_2\text{-NH-})$

was added.

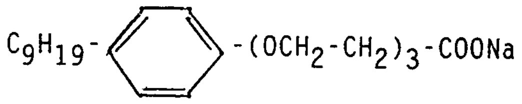
EXAMPLE 6

Instead of gelatin per 100 g of silica 13 g of polyethyleneoxide ("Polyox WSR N3000", trademarked product from Union Carbide) was added, having recurring units corresponding to the formula

$(\text{-CH}_2\text{-CH}_2\text{-O-})$ (M.W. = ca. 600 +/- 100)

EXAMPLE 7

Per 100 g of silica a mixture was used of 6.6 g of polyethylene imine (see example 6) and 32 g of

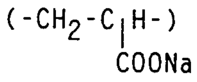


EXAMPLE 8

A solution of 32 g of the organic sodium salt of example 7 (thus without polyethylene imine) was used as a flocculating agent per 100 g of silica.

EXAMPLE 9

Same amount of product as in example 8, mixed with 13 g of polyacrylic acid (sodium salt). This product is known as "LYTRON 889", which is a trademarked product of Monsanto having recurring units of the formula:



$$(\text{-CH}_2\text{-}\underset{\text{COONa}}{\text{C}}\text{H-})$$

For each example the velocity of sedimentation was measured and expressed in cm.min^{-1}. Together with a qualitative judgement of turbidity (clear, light cloudy, very cloudy) indicated respectively by the abbreviations C-LC-VC the results are represented in Table I. After the flocculation and before each washing procedure pH has been adjusted to a value of 2.5 to 3.0 as described above.

TABLE I

Sedimentation velocity (cm.min^{-1}) and turbidity (C-LC-VC)						
Example No.	Mother lye		1st washing		2nd washing	
1	20	C	20	C	15	C
2 (comp.)	0	VC	-	-	-	-
3	8	LC	9	LC	7,5	LC
4 (comp.)	8	VC	10	VC	15	VC
5	7	C	6	LC	4	LC
6	6	LC	3	LC	1,5	VC
7	8	LC	6	LC	1,5	VC
8	5	LC	4	LC	2	LC
9	5	C	4	LC	2	LC

Obviously the best results can be obtained using the inert gelatin of example I. Increasing the number of washing turns, resulting in a higher degree of desalting for the emulsion, gives rise to a decreasing sedimentation velocity. Acceptable results can also be obtained with polyethylene imine. The comparative example II (without flocculating agent) shows that a very stable colloid is formed in accordance with EP 0392092. Even after 60 hours coagulation is hardly observed. Addition of an excess of gelatin (example 4) shows a colloid which remains in a peptised form.

An illustration of the effectiveness with which the flocculation takes place can be given by the analysis of the mother lye and the supernatant liquid, obtained after each washing procedure. The amount of silica (in mg.l^{-1}) is given in Table II for the vessel, determined after having added for comparison purposes water to the starting volume before the precipitation in such an amount that a volume corresponding to the end volume of the precipitation is reached (for example 1 in Table I this means to about an end volume of 800 ml). Besides this comparative example, an analytical determination was executed for the supernatant liquid after the first to the fourth washing procedure.

TABLE II : Analytically determined amount of silica in the vessel, in the mother lye and after washing, being expressed in mg Si pro liter.

Sample	I (starting vessel)	II (mother lye)	III (1st washing)	IV (2nd washing)	V (3rd washing)	VI (4th washing)
mg Si pro liter	690	8.9	3.4	1.5	0.8	0.6

Table II is illustrating clearly that silica is quantitatively adsorbed at the silver halide crystal surface, the losses of silica being limited to between 1 and 2 % in the mother lye and even less than 0.5 % after washing. The flocculation procedure can thus be considered to be quantitative and reliable.

Claims

1. A method of preparing a light-sensitive silver halide emulsion comprising the steps of precipitating silver halide in the presence of colloidal silica serving as a protective colloid, coagulation washing the precipitate formed and redispersing the silver halide emulsion, characterised in that the coagulation takes place in the presence of a polymer capable of forming hydrogen bridges with the silica, in an amount sufficient to form coagulable aggregates with the silica particles.

2. The method according to claim 1, wherein the polymer forming hydrogen bridges, acting as a

flocculating agent is gelatin, polyethylene oxide, polyethylene imide, polyacrylic acid, polyacetic acid, polyvinyl alcohol or polystyrene sulphonic acid or a combination of two or more of these agents.

3. The method according to claim 1 or 2, wherein the flocculating agent is present in an amount of 1 to 40% by weight versus silica sol.

4. The method according to claim 3, wherein the flocculating agent is gelatin and is present in an amount of 10 to 40% by weight versus silica sol.

5. The method according to any of the preceding claims, wherein the colloidal silica has a specific surface area between 200 and 600 m2/g.

6. The method according to any of the preceding claims, wherein the pH value is adjusted to a value between 1.0 and 4.0 before and after addition of the flocculating agent and after each washing step.

7. The method according to claim 6, wherein the pH value is adjusted to a value between 2.5 and 3.0.

8. The method according to any of the preceding claims further including the step of redispersing the precipitated silver halide by addition of colloidal silica.

9. The method according to any of claims 1 to 8, including the step of redispersing the precipitated silver halide by addition of gelatin.

10. The method of preparing a light-sensitive silver halide emulsion comprising the following steps:
a.Precipitating silver halide in aqueous silica medium having a pH above 4.
b.Adjusting the pH of the silver halide emulsion to a value of 1.0 to 4.0.
c.Adding to the emulsion vessel a hydrogen-bridge forming polymer as a focculating agent.
d.Permitting the formation of aggregates after hydrogen-bridge formation.
e.Removing the clear supernatant liquid.
f.Washing the flocculate.
g.Readjusting the pH to a value of 1.0 to 4.0.
h.Removing the clear supernatant liquid.
i.Repeating procedure f to h if necessary to meet the desirable pAg-value demands.
j.Causing redispersion of the flocculate by adding a protective colloid or hydrogen-bridge forming polymer.

11. The method according to any of the claims 1 to 10 further including the steps of chemical and/or spectral sensitization and coating of the emulsion on a support to form a photographic material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 20 1426

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,Y	EP-A-0 392 092 (AGFA-GEVAERT N.V.) * claims 1,5; page 6, example 1; page 10, comparative examples *	1-11	G 03 C 1/04
Y	GB-A-2 184 559 (FORTE FOTOKEMIAI IPAR) * claims; page 4, lines 18-27 *	1-11	
A	FR-A-2 017 463 (AGFA-GEVAERT AG) * page 10, lines 30-35; claims *	1,2,10, 11	
A	FR-A-2 013 285 (AGFA-GEVAERT AG) * page 5, lines 15-29; claims *; & GB - A - 1276894 (cat. D)	1,10	
A	GB-A-2 085 180 (AGFA-GEVAERT AG) * page 9, lines 1-40; claim 7 *	1,2,10	
A	US-A-4 001 022 (MINNESOTA MINING AND MANUFACTURING COMPANY) * claims; column 5, lines 30-37 *	1	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)** G 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	13-02-1992	STOCK H

CATEGORY OF CITED DOCUMENTS

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