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⑤④ **Method of preparing light-sensitive silver halide emulsions.**

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⑤⑥ References cited :  
**FR-A- 1 364 027  
US-A- 3 637 391  
US-A- 3 895 950  
US-A- 4 001 022**

**EP 0 392 092 B1**

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## Description

This invention relates to methods of preparing light-sensitive silver halide emulsions, and to photographic materials incorporating layers of such emulsions.

5 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 is added and the emulsion is subjected to chemical ripening.

10 The most commonly used protective colloid is gelatin. Although possessing many advantages, the conventional gelatino-silver halide emulsion layers undergo considerable swelling and subsequent shrinkage consequent upon absorption and release of processing liquids during image processing. This lack of dimensional stability under processing conditions can adversely affect image quality. Moreover, due to their rather slow absorption and release of the processing liquids, such conventional gelatino-silver halide layers cannot meet the rapid processing criteria which are often demanded. This is notwithstanding the fact that rapid processing  
15 can to some extent be promoted by using light-sensitive photographic materials which incorporate silver halide developing agents in or in water-permeable relationship to the light-sensitive layer and using a two-step development process comprising an activating and stabilising step instead of the conventional development, fixing and washing steps. Stabilization processing is described in for example US. Patent 4 030 924 and "Two bath rapid stabilization Process" published in "British Journal of Photography" Vol. 114, No. 5583, July 21, 1967, pp. 620-621, 625.

20 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.

25 Another substance proposed in the prior art as protective colloid binder in silver-halide emulsions is colloidal silicic acid. 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 silicic acid sol as binder have less tendency to swell on treatment with aqueous processing liquids than conventional gelatino-silver halide emulsion layers of the same thickness. United States Patent 4 001 022 discloses photographic elements which are described as suitable for rapid processing and which comprise a support bearing an acidic developer layer and a basic gelatino-silver halide emulsion layer, both of which layers contain a substantial amount of  
35 colloidal silica. The binder in which the silver halide is dispersed comprises by weight about 6 to 40 percent of gelatin, the remainder being colloidal silica.

40 While the use of silicic acid sol as a protective colloid reduces swelling of light-sensitive silver halide layers during liquid processing, the extent of that advantage has hitherto been limited by the need for the concentration of the silicic acid sol to be restricted in order to avoid making the emulsions physically unstable. The instability of silicic acid sols when used as protective colloid binder for silver halide is recognised in United States Patent 3 637 391. It is disclosed in that patent that if a silicic acid sol of too high a concentration is used, agglomeration occurs when a reaction mixture of alkali metal and silver salts is added to the sol. In order to oppose this agglomeration the patent proposes treatment of the silicic acid sol with ethanol, the addition of a homo or  
45 co-polymer of sufficiently water soluble monomer(s) or the polymerisation of such monomer(s) in situ in the silicic acid sol. However the patent recommends that the precipitated emulsion be redispersed in gelatin before being chemically ripened and that the concentration of the silicic acid sol in the final emulsion should not be more than 20% and preferably not more than 10% by weight.

50 The necessity to restrict the concentration of the silicic acid sol 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.

An object of the present invention is to enable the proportion of silicic acid sol used as a protective colloid in the preparation of silver halide emulsions to be substantially increased without resulting in unacceptable physical instability of the emulsion.

55 According to the present invention there is provided a method of preparing a light-sensitive silver halide emulsion by precipitating silver halide in the presence of colloidal silicic acid serving as protective colloid, characterised in that the precipitation takes place in the presence of an onium compound, except for ammonium bromide.

It has been found from a range of experiments using a variety of onium compounds that they have an emul-

sion-stabilising effect when used as additive in the preparation of light-sensitive silver halide emulsions by precipitating the silver halide in a protective colloid consisting of or comprising colloidal silicic acid. The stabilising effect can be demonstrated by a simple sedimentation test as hereinafter described. The invention therefore makes it possible to form on a photographic support a light-sensitive emulsion layer with a more favourable combination of the properties of water-permeability and dimensional stability during wet development processing and subsequent drying. Such a combination of properties is very desirable in the case of photographic materials for rapid development processing.

In preferred embodiments of the invention, at least 75% by weight of the protective colloid used in the silver halide precipitation step consists of silicic acid sol. In the most preferred embodiments, such protective colloid consists entirely of such sol. In the case that said colloid consists entirely of silicic acid sol, light-sensitive layers which have the maximum dimensional stability benefit derivable from the use of silicic acid sol as binder can be formed directly from the precipitated emulsion after it has been ripened and washed.

However, it is to be understood that the invention is not restricted to methods wherein silicic acid sol is used as the sole protective colloid in the precipitation of the silver halide. The protective colloid used in that precipitation can comprise silicic acid sol and a proportion of some other binder known as such in the photographic art. In particular, the protective colloid can comprise silicic acid sol and gelatin.

If desired, additional silicic acid sol can be added to the emulsion after the precipitation of the silver halide, e.g. during the subsequent redispersion of the emulsion.

It is also possible to add gelatin at the stage of redispersion of the emulsion.

The invention includes light-sensitive material comprising a support bearing at least one light-sensitive silver halide emulsion layer which incorporates silicic acid sol as a protective colloid binder, characterised in that said layer further comprises an onium compound, except for ammonium bromide. The protective colloid binder of said emulsion layer preferably comprises at least 75% by weight of silicic acid sol, and most preferably it consists entirely of such sol.

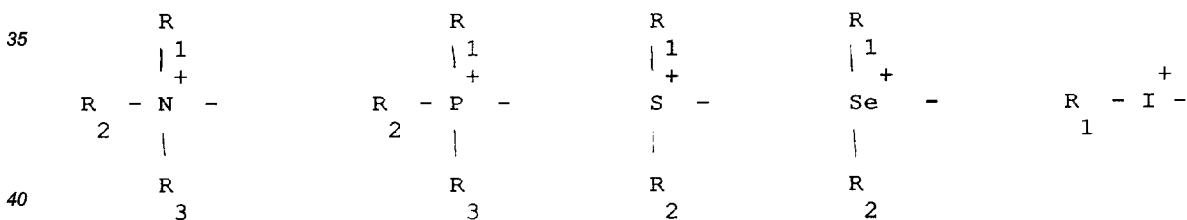
As already indicated, a wide range of onium compounds have been tested and have been found to be effective stabilisers for the purpose in view. The preferred onium compounds according to the present invention can be represented by the following general formulae :



wherein

X<sup>-</sup> represents an anion and

A<sup>+</sup> represents an onium ion selected from any of the following general formulae :



wherein :

each of R<sub>1</sub> and R<sub>3</sub> (same or different) represents hydrogen, an alkylgroup, a substituted alkyl group, a cycloalkyl group, an aryl group or a substituted aryl group,

R<sub>2</sub> represents any of the said groups represented by R<sub>1</sub> and R<sub>3</sub> or the atoms necessary to close a heterocyclic nucleus with either R<sub>1</sub> or R<sub>3</sub>,

the said onium ion being linked

- 1) to a polymer chain, or
- 2) via a bivalent organic linking group e.g., -O-, -S-, -SO<sub>2</sub>-, ... to any other of such onium structure, or
- 3) directly to any of the groups represented by R<sub>1</sub> except for hydrogen.

Suitable examples of onium compounds are disclosed in U.S. Patent 3,017,270.

In said specification suitable examples are mentioned of trialkyl sulfonium salts, polysulfonium salts, tetraalkyl quaternary ammonium salts, quaternary ammonium salts in which the quaternary nitrogen atom is a part of a ring system, cationic polyalkylene oxide salts including e.g. quaternary ammonium and phosphonium and bis-quaternary salts.

Onium salt polymers whereby the onium group may be e.g. an ammonium, phosphonium or sulphonium group, are disclosed in U.S. Patent 4,525,446.

In order to provide stabilization of the precipitated silver halide when silicic acid sol is used as protective colloid, the concentration of onium compound should preferably be not less than  $0.5 \times 10^{-3}$  mol of onium compound and preferably be not higher than  $5 \times 10^{-3}$  mol of onium compound per 90g of  $\text{SiO}_2$ .

5 The usual silicic acid sols are suitable for the process according to the invention, regardless of whether the silicic acid has been prepared by a wet decomposition process or a pyrogenic process.

Suitable silicic acid sols are commercially available such as the "Syton" silica sols (a trademarked product of Monsanto Inorganic Chemicals Div.), the "Ludox" 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 "Kieselsool, Types 100, 200, 300 and 600" (trademarked product of Bayer AG).

10 Preferably the colloidal silicic acid used has a specific surface area between 200 and 400  $\text{m}^2/\text{g}$ . When deciding upon the appropriate amount of colloidal silicic acid to be used during the precipitation of the silver halide, the specific surface area of the selected type of colloidal silicic acid should be taken into account.

Suitable results are also obtained when silicic acid sols containing up to 20 percent by weight of aluminium oxide related to the solid content, are used.

15 The process of the invention is suitable for the preparation of silver halide emulsions, the halide composition of which is not specifically limited and may be any composition selected from i.a. chloride, bromide, iodide, chlorobromide, bromiodide, and chlorobromiodide. The content of silver iodide is equal to or less than 20 mol%, preferably equal to or less than 5 mol%, even more preferably equal to or less than 3 mol%.

20 The photographic silver halide emulsions used according to the present invention can be prepared by mixing the halide and silver solutions in partially or fully controlled conditions of temperature, concentrations, sequence of addition, and rates of addition. The silver halide can be precipitated according to the single-jet method, the double-jet method, or the conversion method.

25 Suitable preparation methods are described e.g. by 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 by in V.L. Zelikman et al in "Making and Coating Photographic Emulsion", The Focal Press, London (1966).

30 The silver halide particles of the photographic emulsions used according to the present invention may have a regular crystalline form such as a cubic or octahedral form or they may have a transition form. They may also have an irregular crystalline form such as a spherical form or a tabular form, or may otherwise have a composite crystal form comprising a mixture of said regular and irregular crystalline forms.

35 The silver halide grains may have a multilayered grain structure. According to a simple embodiment the grains may comprise a core and a shell, which may have different halide compositions and/or may have undergone different modifications such as the addition of dopes. The silver halide crystals can be doped e.g. with  $\text{Rh}^{3+}$ ,  $\text{Ir}^{4+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ . Besides having a differently composed core and shell the silver halide grains may also comprise different phases inbetween.

Further, during precipitation grain growth restrainers or accelerators may be added.

Two or more types of silver halide emulsions that have been prepared differently can be mixed for forming a photographic emulsion for use in accordance with the present invention.

40 The average size of the silver halide grains may range from 0,01 to 7  $\mu\text{m}$ , preferably from 0,01  $\mu\text{m}$  up to 5  $\mu\text{m}$ .

The size distribution of the silver halide particles of the photographic emulsions to be used according to the present invention can be homodisperse or heterodisperse. A homodisperse size distribution is obtained when 95% of the grains have a size that does not deviate for more than 30% from the average grain size.

45 The emulsion can be desalted by ultra-centrifugal techniques, by dialysis, which is a preferred method for the emulsions prepared in accordance with the present invention, and ultrafiltration, by flocculation and redispersing, etc.

50 The light-sensitive silver halide emulsion can be a so-called primitive emulsion, in other words an emulsion that has not been chemically sensitized. However, the light-sensitive silver halide emulsion 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 rhodamines. 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 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.

The silver halide emulsion for use in accordance with the present invention may comprise 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), Chapitre VI.

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

The photographic element of the present invention may further comprise various kinds of surface-active agents in the photographic emulsion layer or in at least one other hydrophilic colloid layer. Suitable surface-active agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylene glycol condensation products, polyethylene glycol alkyl ethers or polyethylene glycol alkylaryl ethers, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivatives, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agents comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as alkylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Such surface-active agents can be used for various purposes e.g. as coating aids, as compounds preventing electric charges, as compounds improving slidability, as compounds facilitating dispersive emulsification, as compounds preventing or reducing adhesion, and as compounds improving the photographic characteristics e.g. higher contrast, sensitization, and development acceleration.

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

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

In case the emulsion has been prepared in accordance with the most preferred mode of application of the invention, i.e. precipitation in the presence of silicic acid sol only, and if the ratio by weight of silicic acid sol over silver halide exceeds 0.5 and preferably exceeds 1.0, the addition of supplemental hardening agents is not required to the emulsion so as to form photographic materials.

So as to reach the weight ratios of 0.5 and preferably 1.0 of silicic acid sol over silver halide, apart from silicic acid sol being added during redispersion of the emulsion, supplemental silicic acid sol should be added

shortly before coating the silver halide emulsion concerned on a suitable substrate such as, preferably, a thermoplastic resin e.g. polyethyleneterephthalate.

If, however, apart from the silicic acid sol (an) additional protective colloid 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.

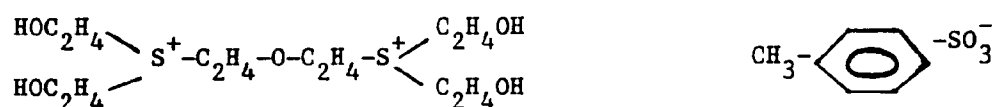
In general, the average particle size of spacing agents is comprised between 0.2  $\mu\text{m}$  and 10  $\mu\text{m}$ . Spacing agents can be soluble or insoluble in alkali. Alkali-insoluble spacing agents usually remain permanently in the photographic element, whereas alkali-soluble spacing agents 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.

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

### Example I

A photographic emulsion was prepared and coated on a support according to the following procedure : 300 ml of 30 % silica sol, 'Kieselso 300F' (trademarked product of Bayer A.G.), 100 ml of 1 % solution of a stabilizing sulfonium compound corresponding to the following formula :



and demineralised water up to a total volume of 2000 ml were mixed with constant stirring in a 12 l stainless steel vessel. Then the temperature was stabilised at 20°C, the pH adjusted to 3.0 by the addition of a sufficient amount of 6N sulfuric acid and the pAg was adjusted to 9.0.

Precipitation in the above medium took place in two subsequent stages under balanced double jet conditions (2.94 mol potassium bromide and 2.94 mol silver nitrate) and was pAg-controlled by regulating the flow of the alkali metal salt. The latter was realised according to the automated electronic control apparatus for silver halide preparation disclosed by Claes and Peelaers in Photographische Korrespondenz 102, Band Nr. 10/1967, pp. 162.

The following two stages took place during the precipitation :

- first a crystallisation stage during a period of five minutes under a constant flow of 20 ml/min, followed by
- a ripening stage during a period of twenty five minutes under a steadily increasing flow of 20 up to 52 ml/min.

The above two stages took place under a pH which was constantly held at 3.0, a pAg constantly held at 9.0, with constant stirring and whereby the temperature of the silver bromide dispersion was stabilised at 20°C.

Hereafter the emulsion contained approximately 110 g of silver nitrate per kg of the dispersion.

Thereupon the dispersion was subject to dialysis in a Holoflow dialysing tube type F60 (trademark produced of Fresenius AG, D6370 Oberursel, F.R. Germany, dialyse-volume of 75 ml) forming part of a closed circuit wherein the dispersion was circulated. In a first step the dispersion showing an electrical conductivity

of 100 mS was concentrated within 30 min to half of its volume whereupon dialysis continued for another 30 min period. The desalted dispersion then showed an electrical conductivity of approximately 2 mS and contained 225 g of silver nitrate per kg solution.

5 The ratio of silica sol over silver nitrate was then 0.18, whereupon it was increased up to 0.2 by the addition of a sufficient amount of 30 % silica sol.

The dispersion was subjected to chemical ripening during 30 min at a constant pH level of 5.0 and pAg value of 9.0 at a stabilised temperature of 20°C by addition of  $2.2 \times 10^{-6}$  mol of  $\text{Au}^{3+}$  per 50 g of silver nitrate and  $1.26 \times 10^{-4}$  mol of  $\text{S}_2\text{O}_3^{2-}$  per 50 g of silver nitrate.

10 Then the ratio of silica sol over silver nitrate was increased up to 0.5 by the addition of supplemental silica sol and the dispersion was manually coated in a thermo-stabilised coating table at 50°C, on a support consisting of polyethylene coated paper carrying a gelatine containing substratum layer (comprising 0.4 g of gelatin per square meter) is coated.

Exposure during 10 sec by a tungsten bulb through a grey step wedge (with constant factor 0.2) after processing yields seventeen visually discernible density gradations in the photographic strip.

15 The light intensity as measured with a MAVOLUX light meter, type 'Electronic' (trademarked product of Gossen GmbH, D8520 Erlangen, F.R. Germany) on the strips amounts to 1350 Lux. Processing took place in a conventional metal hydrochinon developer (buffered at a pH of 10.2 with sodium carbonate) during one minute, followed by fixation during 30 seconds in a 0.9 molar ammonium thiosulfate bath stabilised at a pH of 5, followed by rinsing in water during 30 seconds.

20 Example II (comparative example I)

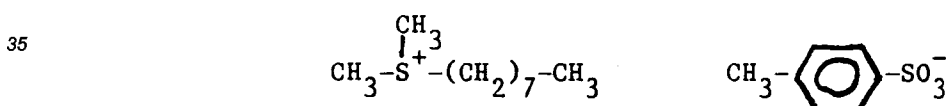
A photographic emulsion was prepared according to the procedure described in Example I; however no stabilising compound was used. The stability of the precipitated silver halide was extremely poor and heavy sedimentation occurred.

Examples III to XVII

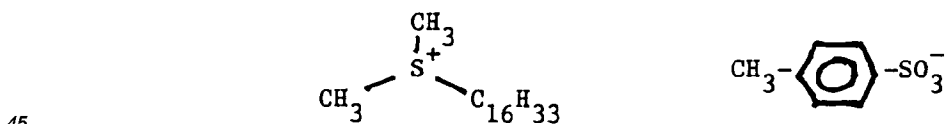
30 Photographic emulsions were prepared according to the procedure described in Example I, except that the following compounds were used as stabilising compound :

Example III : same stabilising compound as example I,

Examples IV and V : a monosulfonium compound according to the following structural formula :



40 Examples VI and VII : a monosulfonium compound according to the following structural formula :

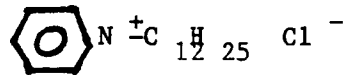


Examples VIII and IX : a iodonium compound according to the following structural formula :

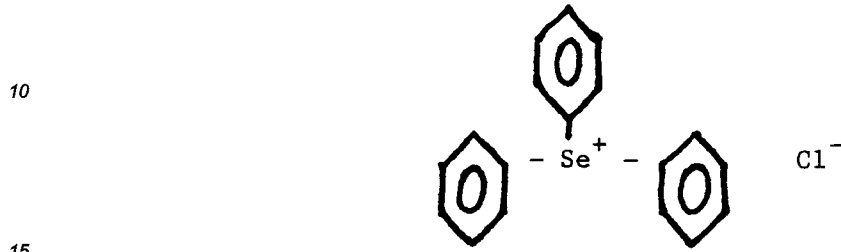


Examples X and XI : a quaternary ammonium compound (pyridine-derivative) according to the following structural formula :

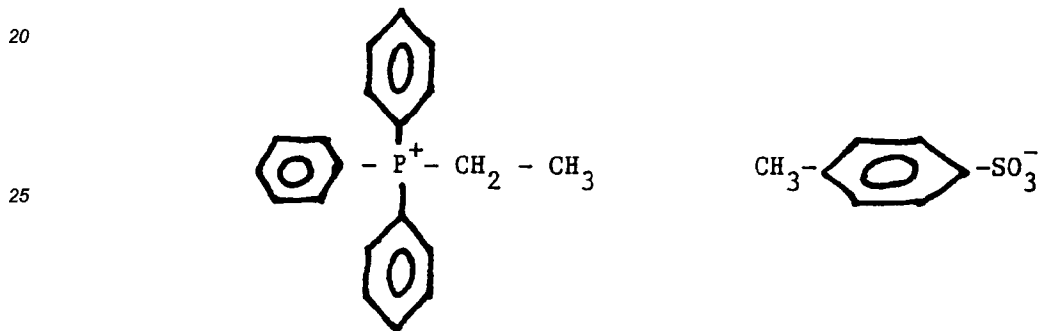
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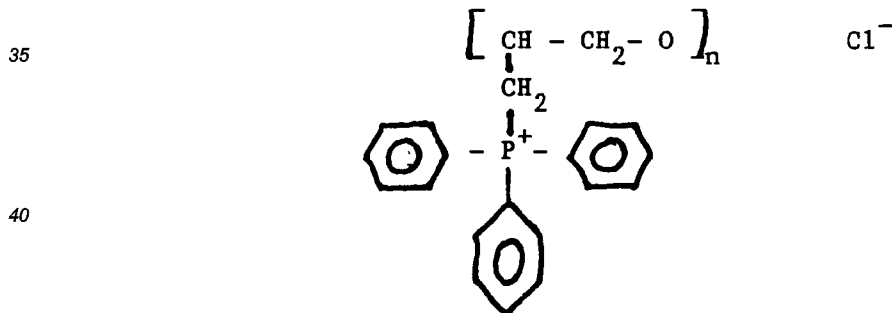
5 Examples XII and XIII : a selenonium compound according to the following structural formula :



Examples XIV and XV : a phosphonium compound according to the following structural formula :



Examples XVI and XVII : a polyphosphonium compound according to the following structural formula, n being 22 :



45 In the examples I and II the precipitation took place at a stabilised temperature of 20°C. Since the stability of a silica sol decreases with increasing temperature, the silver halide precipitation in all the other examples III to IXX has been carried out at a temperature of 60°C so that the stabilizing effect of the onium compound could better be evaluated.

50 In table I the concentrations at which the different onium-stabilising compounds are used are set forth, as well as the results of the precipitation step in terms of stability of the suspension and degree of sedimentation, if any.

The concentrations of stabilising compound set forth in Table I are all expressed in 10<sup>-2</sup> mol of stabilising compound per 90 g of silica sol. The values set forth for stability are the results of measurements resp. calculations in accordance with the following procedure.

55 At the end of the precipitation step a 10 ml sample of emulsion is brought into a 10 ml graduated cylinder. The stability of the emulsion is then measured as a function of time by checking the visubility of a sign (e.g. an arrow) which is affixed at the rear of said graduated cylinder. When the sign is visual, the level till which the visubility reaches is noted. The evolution of this level as a function of time is taken as a measure for the

stability.

The values measured in accordance with the preceding procedure are then plotted in a graph as a function of time as illustrated in figure 1. In the abscis the time (expressed in minutes) is set forth whereas in ordinate the level is noted. The ratio of the surface under the graph for a period of 30 minutes over the surface of a constant level of 10 held for a period of 30 minutes is regarded as a measure of stability.

The stability is then expressed as follows :

$$\text{stability} = \frac{\int_{t=0}^{t=30} \text{level (t) dt}}{10 \times 30}$$

From the above it is apparent that the closer the stability value approaches 1, the higher the stability of the emulsions.

If the value for stability equals 0, the stability is minimal, whereas if the value equals 1, the stability is maximal.

The values for stability obtained in accordance with the above measurements and calculations should be interpreted as follows :

- value equalling 1.00 : excellent stability, at least for a period of 30 minutes but in most cases for more than two hours
- values between 1.00 and 0.97 : moderate stability
- values under 0.97 : insufficient stability (not suited for further processing).

The values set forth for sedimentation should be interpreted as follows :

- : no formation of sediment
- + : some sedimentation
- ++ : heavy sedimentation
- +++ : very heavy sedimentation.

### Example XVIII

A photographic tabular grain emulsion was prepared and coated on a support according to the following procedure :

2000 ml of demineralised water, 83 ml of 30 % Kieselsol 300F (trademarked product of Bayer AG), 18.5 ml of a 1 % solution of the stabilising compound as described in Example I were mixed under constant stirring in a 12 l stainless steel vessel. After heating up to 70°C (under continuous stirring), 1045 ml of demineralised water were added, the pH of the solution was brought to 3.0 by the addition of 6N sulfuric acid, and the pAg was brought to 9.49 by addition of a 2.94 molar solution of potassium bromide.

Precipitation in the above medium took place in two subsequent stages :

1) under balanced double jet conditions during a period of 18 sec flows of silver nitrate and potassium bromide were added at a rate of 25 ml/min; pAg control was effected according to the same method as described for example I. Hereafter physical ripening took place during 15 min at 70°C; then over a period of 5 minutes a silica sol solution according to the following composition was added dropwise : 217 ml of 30 % silica sol, 36 ml of a 1 % solution of the stabilising compound described in Example I, and 460 ml of demineralised water, the pH of the solution being adjusted to 3.0.

2) the pAg of the solution was adjusted to 9.05, then under balanced double jet conditions and with the pAg control method as described hereinbefore, the flows of silver nitrate and potassium bromide over a period of 64 min and 10 sec were steadily increased from 5 to 24.4 ml/min.

Hereafter the dispersion was cooled from 70 to 20°C under constant stirring and further washed by dialysis as described in Example I. The aspect ratio was measured and found to be between 2,5 and 6, but if so desired may be increased up to 12.

The results in terms of stability and possible sedimentation of the photographic emulsion obtained according this procedure are also set forth in Table I.

### Comparative examples II to IV

A photographic emulsion was prepared according to the procedure described in Example I; however, in-

stead of the sulfonium compound of said example the following compounds were used (the use of these compounds is suggested for precipitation to take place in the absence of gelatin and in the presence of silica in the US Patent 3,637,391 cited hereinbefore) :

in comparative example II : ethanol (96 %)

5 in comparative example III : polyvinylalcohol

in comparative example IV : polyvinylalcohol

in comparative example V : polyacrylamide

In table II the results of said comparative examples in terms of stability and sedimentation are set forth. The figures, resp. values for stability and sedimentation set forth in Table II are the result of measurements resp. calculations according to the same procedure as these set forth in Table I, and should be interpreted accordingly.

The polyvinylalcohols used in the comparative examples III and IV show an intrinsic viscosity of 5, resp. 28, when measured at 20°C in a 4 % by weight aqueous solution of said polyvinylalcohol.

From the above examples it is apparent that a fully stabilised silver halide dispersion in silica sol without sedimentation can only be achieved when a stabilising compound as described and claimed according to the present invention is used.

20 TABLE I

example no.	Concentration of stabilizing compound	Stability	Sedimentation
I	0.15	1.00	-
II (comp. ex. I)	none	0.25	+++
III	0.15	1.00	-
30 IV	0.3	1.00	+
V	3	0.97	+/-
VI	0.3	1.00	-
35 VII	3	0.71	-
VIII	3	0.97	-
IX	0.3	1.00	-
X	3	0.82	-
40 XI	0.3	1.00	-
XII	3	0.97	-
XIII	0.3	1.00	-
45 XIV	3	0.97	-
XV	0.3	1.00	-
XVI	3	0.91	-
XVII	0.3	1.00	-
50 XVIII	1.0	1.00	-

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TABLE II

Comparative example no.	Concentration of art stab. comp.	Stability	Sedimentation
II	200 ml	1.00	++
III	1.8 g	1.00	+++
IV	1.8 g	1.00	++
V	4 g	1.00	++

### Claims

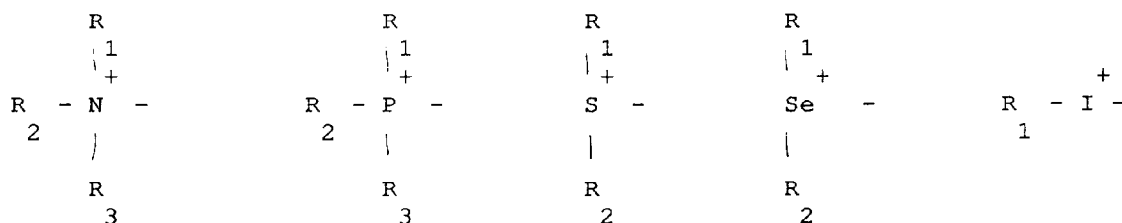
1. A method of preparing a light-sensitive silver halide emulsion including the step of precipitating silver halide in the presence of colloidal silicic acid serving as protective colloid, characterised in that the silver halide precipitation takes place in the presence of an onium compound, except from ammonium bromide.
2. The method according to claim 1, wherein the onium compound is a compound according to the following general formulae :



wherein

$X^-$  represents an anion and

$A^+$  represents an onium ion selected from any of the following general formulae :



wherein :

each of  $R_1$  and  $R_3$  (same or different) represents hydrogen, an alkyl group, a substituted alkyl group, a cycloalkyl group, an aryl group or a substituted aryl group,

$R_2$  represents any of the said groups represented by  $R_1$  and  $R_3$  or the atoms necessary to close a heterocyclic nucleus with either  $R_1$  or  $R_3$ ,

the said onium ion being linked

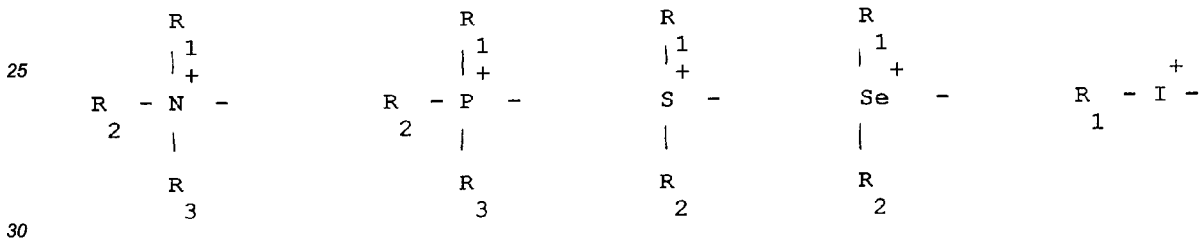
- 1) to a polymer chain, or
- 2) via a bivalent organic linking group to any other of such onium structure, or
- 3) directly to any of the groups represented by  $R_1$  except for hydrogen.

3. The method as claimed in claims 1 or 2 wherein the onium compound is present in an amount corresponding to at least  $0.5 \times 10^{-3}$  mol per 90 g of silicic acid sol.

4. The method according to any of the preceding claims wherein the colloidal silicic acid has a specific surface area between 200 and 400 m<sup>2</sup>/g.
5. The method according to any of the preceding claims, wherein in addition to the colloidal silicic acid gelatin is present as additional protective colloid.
6. The method as claimed in claim 5 wherein at least 75% by weight of the protective colloid used in the silver halide precipitation step consists of colloidal silicic acid.
7. The method as claimed in any of the preceding claims further including the step of redispersing the precipitated silver halide in the presence of colloidal silicic acid.
8. A light-sensitive silver halide material comprising a support bearing at least one light-sensitive silver halide layer which incorporates a silicic acid sol as a protective colloid binder and an onium compound, except for ammonium bromide.
9. Light-sensitive material as defined in claim 8 wherein said onium compound corresponds to the following general formula :



wherein X<sup>-</sup> represents an anion and A<sup>+</sup> represents an onium ion selected from any of the following general formulae :



wherein :

- each of R<sub>1</sub> and R<sub>3</sub> (same or different) represents hydrogen, an alkyl group, a substituted alkyl group, a cycloalkyl group, an aryl group or a substituted aryl group,
- R<sub>2</sub> represents any of the said groups represented by R<sub>1</sub> and R<sub>3</sub> or the atoms necessary to close a heterocyclic nucleus with either R<sub>1</sub> or R<sub>3</sub>, the said onium ion being linked
- 1) to a polymer chain, or
  - 2) via a bivalent organic linking group to any other of such onium structure, or
  - 3) directly to any of the groups represented by R<sub>1</sub> except for hydrogen.

10. Light-sensitive material as defined in claim 8 or 9 wherein the onium compound is present in an amount corresponding to at least 0.5 × 10<sup>-3</sup> mol per 90 g of colloidal silicic acid.

### Patentansprüche

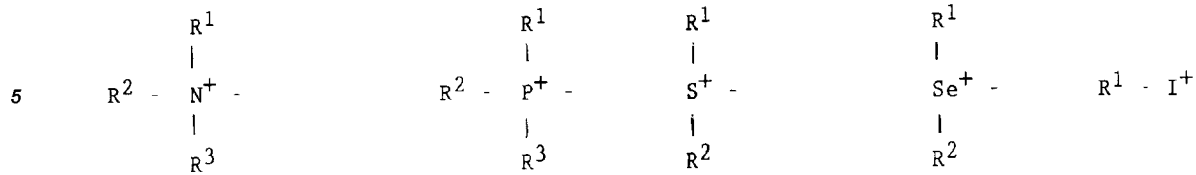
1. Ein Verfahren zur Bereitung einer lichtempfindlichen Silberhalogenidemulsion einschließlich der Fällung von Silberhalogenid in Anwesenheit einer kolloidalen Kieselsäure, die als Schutzkolloid dient, dadurch gekennzeichnet, daß die Fällung von Silberhalogenid in Anwesenheit einer Oniumverbindung, Ammoniumbromid ausgenommen, stattfindet.
2. Das Verfahren gemäß Anspruch 1, dadurch gekennzeichnet, daß die Oniumverbindung der nachstehenden allgemeinen Formel entspricht:



in der bedeuten:

X<sup>-</sup> ein Anion und

A<sup>+</sup> ein Onium-Ion, das aus irgendwelcher der nachstehenden allgemeinen Formeln gewählt wird:



10

in denen bedeuten:

R<sup>1</sup> und R<sup>3</sup> (gleich oder verschieden) je ein Wasserstoffatom, eine Alkylgruppe, eine substituierte Alkylgruppe, eine Cycloalkylgruppe, eine Arylgruppe oder eine substituierte Arylgruppe,

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R<sup>2</sup> irgendwelche der von R<sup>1</sup> und R<sup>3</sup> dargestellten Gruppen, oder die notwendigen Atome zum Schließen eines heterocyclischen Ringes mit entweder R<sup>1</sup> oder R<sup>3</sup>,

wobei das Onium-Ion verbunden ist

20

- 1) mit einer Polymerkette, oder
- 2) über eine zweiwertige organische Verbindungsgruppe mit irgendwelcher anderen derartigen Oniumstruktur, oder
- 3) direkt mit irgendwelcher der von R<sup>1</sup> dargestellten Gruppen, das Wasserstoffatom ausgenommen.

25

3. Das Verfahren gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Oniumverbindung in einem Gehalt anwesend ist, der zumindest mit 0,5 · 10<sup>-3</sup> mol pro 90 g Kieselsäure-Sol übereinstimmt.

4. Das Verfahren gemäß irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die kolloidale Kieselsäure eine spezifische Oberfläche zwischen 200 und 400 m<sup>2</sup>/g hat.

5. Das Verfahren gemäß irgendwelchem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß außer der kolloidalen Kieselsäure Gelatine als zusätzliches Schutzkolloid anwesend ist.

30

6. Das Verfahren gemäß Anspruch 5, dadurch gekennzeichnet, daß zumindest 75 Gew.-% des in der Silberhalogenid-Fällung verwendeten Schutzkolloids aus kolloidaler Kieselsäure besteht.

7. Das Verfahren gemäß irgendwelchem der vorstehenden Ansprüche, das weiterhin das Wiederdispergieren des niedergeschlagenen Silberhalogenids in Anwesenheit kolloidaler Kieselsäure umfaßt.

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8. Ein lichtempfindliches Silberhalogenidmaterial, das einen Träger umfaßt, auf dem sich zumindest eine lichtempfindliche Silberhalogenidschicht befindet, in die ein Kieselsäure-Sol als schützendes Kolloidbindemittel und eine Oniumverbindung, Ammoniumbromid ausgenommen, einverleibt sind.

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9. Ein lichtempfindliches Material gemäß Anspruch 8, dadurch gekennzeichnet, daß die Oniumverbindung der nachstehenden allgemeinen Formel entspricht:

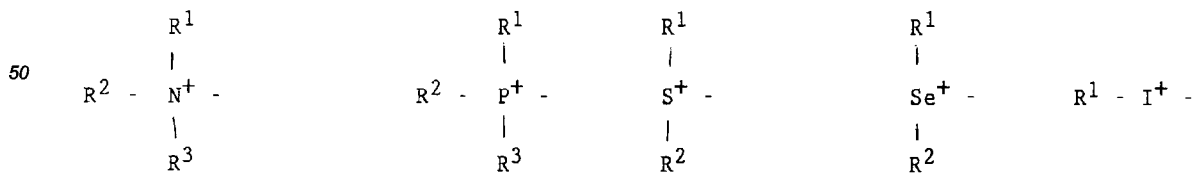


in der bedeuten:

X<sup>-</sup> ein Anion und

45

A<sup>+</sup> ein Onium-Ion, das aus irgendwelcher der nachstehenden allgemeinen Formeln gewählt wird:



55

in denen bedeuten:

R<sup>1</sup> und R<sup>3</sup> (gleich oder verschieden) je ein Wasserstoffatom, eine Alkylgruppe, eine substituierte Alkylgruppe, eine Cycloalkylgruppe, eine Arylgruppe oder eine substituierte Arylgruppe,

R<sup>2</sup> irgendwelche der von R<sup>1</sup> und R<sup>3</sup> dargestellten Gruppen, oder die notwendigen Atome zum Schließen eines heterocyclischen Ringes mit entweder R<sup>1</sup> oder R<sup>3</sup>, wobei das Onium-Ion verbunden ist

- 5
- 1) mit einer Polymerkette, oder
  - 2) über eine zweiwertige organische Verbindungsgruppe mit irgendwelcher anderen derartigen Oniumstruktur, oder
  - 3) direkt mit irgendwelcher der von R<sup>1</sup> dargestellten Gruppen, das Wasserstoffatom ausgenommen.

- 10
10. Ein lichtempfindliches Material gemäß Anspruch 8 oder 9, dadurch gekennzeichnet, daß die Oniumverbindung in einem Gehalt anwesend ist, der zumindest mit 0,5 · 10<sup>-3</sup> mol pro 90 g kolloidale Kieselsäure übereinstimmt.

### Revendications

- 15
1. Un procédé pour la préparation d'une émulsion à l'halogénure d'argent sensible à la lumière, y compris la phase de la précipitation d'halogénure d'argent en présence d'acide silicique colloïdal servant de colloïde protecteur, caractérisé en ce que la précipitation d'halogénure d'argent s'effectue en présence d'un composé onium, excepté le bromure d'ammonium.

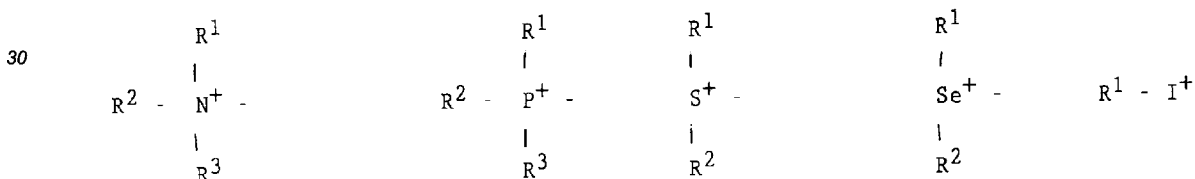
- 20
2. Le procédé selon la revendication 1, caractérisé en ce que le composé onium correspond à la formule générale suivante:



dans laquelle:

25 X<sup>-</sup> représente un anion, et

A<sup>+</sup> représente un ion onium, choisi dans l'une quelconque des formules générales suivantes:



35 dans lesquelles:

R<sup>1</sup> et R<sup>3</sup> (identiques ou différents) représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe alkyle substitué, un groupe cycloalkyle, un groupe aryle ou un groupe aryle substitué,

40 R<sup>2</sup> l'un quelconque des groupes représentés par R<sup>1</sup> et R<sup>3</sup>, ou les atomes nécessaires pour fermer un noyau hétérocyclique avec R<sup>1</sup> ou R<sup>3</sup>, l'ion onium étant lié

- 1) à une chaîne polymère, ou
- 2) via un groupe de liaison organique bivalent à n'importe quelle autre d'une telle structure onium, ou
- 3) directement à l'un quelconque des groupes représentés par R<sup>1</sup>, excepté l'atome d'hydrogène.

- 45
3. Le procédé selon la revendication 1 ou 2, caractérisé en ce que le composé onium est présent dans un taux correspondant à au moins 0,5 · 10<sup>-3</sup> mole par 90 g de sol d'acide silicique.

- 50
4. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'acide silicique colloïdal a une aire de surface spécifique entre 200 et 400 m<sup>2</sup>/g.

5. Le procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que, outre l'acide silicique colloïdal, de la gélatine est présente comme colloïde protecteur additionnel.

- 55
6. Le procédé selon la revendication 5, caractérisé en ce qu'au moins 75 % en poids du colloïde protecteur utilisé dans la phase de précipitation d'halogénure d'argent consiste en acide silicique colloïdal.

7. Le procédé selon l'une quelconque des revendications précédentes comprenant en plus la phase de la redispersion de l'halogénure d'argent précipité en présence d'acide silicique colloïdal.

8. Un matériau à l'halogénure d'argent sensible à la lumière comprenant un support portant au moins une couche à l'halogénure d'argent sensible à la lumière incorporant un sol d'acide silicique comme liant colloïdal protecteur et un composé onium, à l'exception de bromure d'ammonium.

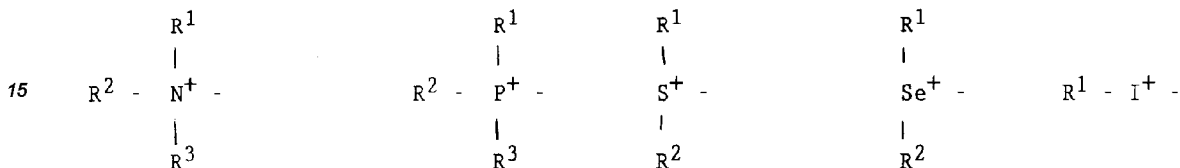
5 9. Un matériau sensible à la lumière selon la revendication 8, caractérisé en ce que le composé onium correspond à la formule générale suivante:



dans laquelle:

X<sup>-</sup> représente un anion, et

10 A<sup>+</sup> représente un ion onium, choisi dans l'une quelconque des formules générales suivantes:



20 dans lesquelles:

R<sup>1</sup> et R<sup>3</sup> (identiques ou différents) représentent chacun un atome d'hydrogène, un groupe alkyle, un groupe alkyle substitué, un groupe cycloalkyle, un groupe aryle ou un groupe aryle substitué,

25 R<sup>2</sup> l'un quelconque des groupes représentés par R<sup>1</sup> et R<sup>3</sup> ou les atomes nécessaires pour fermer un noyau hétérocyclique avec R<sup>1</sup> ou R<sup>3</sup>, l'ion onium étant lié

1) à une chaîne polymère, ou

2) via un groupe de liaison organique bivalent à n'importe quelle autre d'une telle structure onium, ou

3) directement à l'un quelconque des groupes représentés par R<sup>1</sup>, excepté l'atome d'hydrogène.

30 10. Un matériau sensible à la lumière selon la revendication 8 ou 9, caractérisé en ce que le composé onium est présent dans un taux correspondant à au moins 0,5 10<sup>-3</sup> mole par 90 g d'acide silicique colloïdal.

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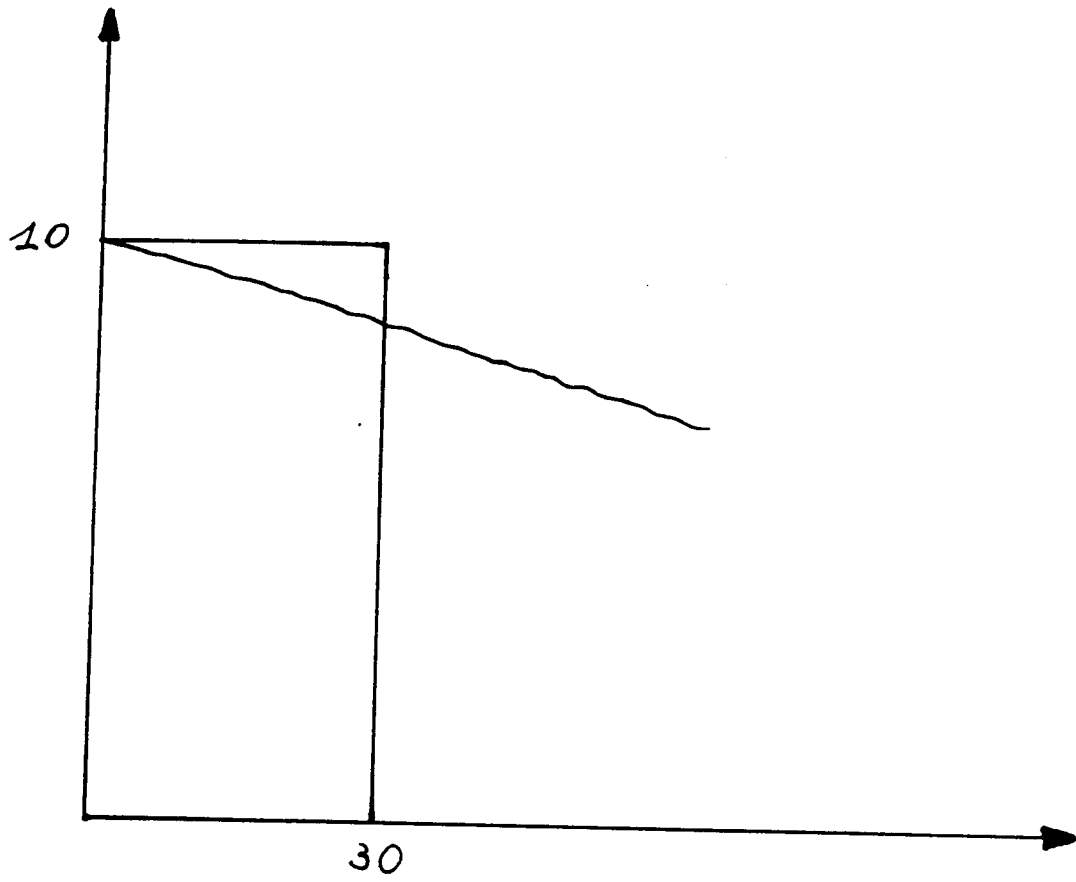


Figure 1 : Representation of stability graph.