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# PHOTOGRAPHIC EMULSIONS CONTAINING A SILANIC SENSITIZER

Russell H. Gray, Red Bank, N. J., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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This invention relates to photography and more particularly to radiation sensitive photographic emulsions and elements. Still more particularly it relates to light-sensitive silver halide emulsions or dispersions and to photographic elements having a layer or layers composed of such emulsions which have in operative association with the emulsions a silanic compound possessing at least one silicon-hydrogen linkage.

An object of this invention is to provide improved photographic silver halide emulsions and emulsion layers. Another object is to provide a practical and economical method of increasing the speed of photographic silver halide emulsions and emulsion layers. A further object is to provide photographic elements including plates, films and papers with silver halide emulsion layers of increased speed or sensitivity. A still further object of the invention is to provide such photographic elements of two or more layers with different degrees of sensitivity in the various layers. Still other objects will be apparent from the following description of the invention.

It has been discovered that if a small amount of a silanic compound possessing at least one silicon-hydrogen linkage is brought into operative association with a light-sensitive silver halide emulsion a beneficial increase in the speed or sensitivity of the emulsion is obtained. The silanic compounds can be brought into operative association with the silver halide grains by incorporating them with the emulsions or by having them in a layer contiguous with the silver halide emulsion layer.

While the invention is useful in improving the speed or sensitivity of photographic silver halide emulsions in general, it is especially useful for improving silver halide emulsions which have a pH on the alkaline side.

In a preferred embodiment of the invention the silanic compounds which possess at least one silicon-hydrogen bond are coated, combined, or adsorbed on the surface of finely divided discrete inert particles which have an average diameter not greater than 10,000 and not less than 1 millimicron. The coated particles have the advantage that they provide a relatively large surface area so that the silanic compound will be brought into operative association or intimate contact with the silver halide grains and by virtue of their size tend to prevent diffusion or wandering in the coated layers. Suitable materials for the discrete inert particles include colorless or white materials, e. g., silicon dioxide of the dense or solid type, inorganic silicates such as magnesium silicate, diatomaceous silicas, sodium aluminum silicate and calcium carbonate, barium sulfate and titanium dioxide, etc., or colored or black particles, e. g., carbon black, lamp black, etc.

The inert particles can be coated by adding an inert solvent solution or dispersion of the silanic compound to the finely divided particles. The amount of silanic compound used, should in general, constitute from 0.1% to 100% of the total weight of the coated particles. In the case of liquid silanic compounds, no solvent is needed and the inert particles and liquid silanic compound can be mixed in suitable proportions so that the latter are coated in an amount between 0.1% and 100% based on the weight of the particles.

In the preferred aspect of the invention, the silanic compounds containing at least one silicon-hydrogen bond are incorporated with the light-sensitive silver halide emulsion prior to coating it as a layer in a photographic element, e. g., a film, plate or paper. This may be accomplished by adding it or a particle coated with it to the



silver halide emulsion or dispersion at some stage during the preparation of or treatment of the emulsion prior to coating. In general, it is more advantageous to incorporate the silanic compound with the emulsion or dispersion subsequent to the attainment of the final or maximum silver halide grain size, e. g., before, during or after the stage of emulsion manufacture termed "remelting," "digestion" or "second or after-ripening."

The invention will be further illustrated but is not intended to be limited by the following examples wherein the emulsions were made and coated under such conditions that no significant amount of actinic light was present.

### *Example 1*

A gelatino silver bromo-chloride emulsion (AgBr=76.2 mol percent, AgCl=23.8 mol percent) was prepared by a procedure which normally yields a normal speed enlarging paper emulsion, but "inert" gelatin and no sensitizing dye was used so that the resultant coated emulsion had a sensitivity of 1/10th to 1/50th of the normal product. Immediately before emulsion "digestion" the silanic compound given in the table below was added to a portion in the quantity as shown on the basis of 1.5 mols of silver halide in the emulsion, the emulsion was then digested at 127° F. for 60 minutes. After this digestion and before coating chrome alum, glycerine, benzotriazole and saponin were added. The resulting emulsions were coated onto a baryta coated paper base to form a thin layer and dried. Samples of these coatings were then exposed to a standard negative in a diffuse-light enlarger so that prints matched for photographic quality were obtained upon development in a solution of the following composition:

| | Grams |
|---|---|
| N-methyl para-aminophenol sulfate | 1.0 |
| Hydroquinone | 4.0 |
| Sodium sulfite | 15.0 |
| Sodium carbonate | 22.5 |
| Potassium bromide | 0.63 |
| Water to make 1.0 liter | |

for 1.5 minutes at 68° F. The results are shown in the following table.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0.01 |
| Silica particles coated with hydrolyzed trichlorosilane | 1.05 | 417 | 0.04 |

The coated silica particles in the above table were made by treating water moistened silica particles having an average particle diameter of 0.015 micron with trichlorosilane which then hydrolyzed to form a coating of $(HSiO_{1.5})_n$ where $n$ is 1 or more which constituted 15 to 20% of the total weight of the coated particle.

### *Example 2*

Inert-gelatin silver bromo-chloride emulsions containing the sensitizing adjuvant given in the table below were made, coated, exposed and processed in the same manner as in Example 1 except that emulsion pH was adjusted to a pH of 8.5 with 0.6M NaOH immediately after the addition of the sensitizer and before digestion.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0.02 |
| Silica particles coated with hydrolyzed trichlorosilane | 1.05 | 858 | 0.06 |

The coated particles contained 0.184 g. of $(HSiO_{1.5})_n$ where $n$ is 1 or greater.

### *Example 3*

Inert-gelatin silver bromo-chloride emulsions containing the adjuvant listed in the table below were made,

coated, exposed and processed in the same manner as described in Example 2.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0.01 |
| Solid silica particles coated with hydrolyzed trichlorosilane | 1.05 | 375 | 0.02 |

The silica particles were coated with $(HSiO_{1.5})_n$ where $n$ is 1 or greater.

*Example 4*

Inert-gelatin silver bromo-chloride emulsions containing the adjuvants listed in the table below were made, coated, exposed and processed in the same manner as described in Example 2.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0 |
| Silica particles coated with hydrolyzed trichlorosilane | 0.095 | 175 | 0 |
| Solid silica particles coated with HO $[C_2H_5(H)SiO]_{6-20}H$ | 0.095 | 155 | 0 |

*Example 5*

Inert-gelatin silver bromo-chloride emulsions containing the adjuvants listed in the table below were made, coated, exposed and processed in the same manner as described in Example 2.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0 |
| Cyclic $[C_2H_5(H)SiO]_4$ | 0.01 | 700 | 0.05 |
| Cyclic $[C_2H_5(H)SiO]_4$ | 0.005 | 350 | 0 |

The $[C_2H_5(H)SiO]_4$ of this example was a cyclic tetramer prepared by the hydrolysis of $C_2H_5(H)SiCl_2$ and subsequent condensation of the intermediate to the cyclic tetramer.

*Example 6*

Inert-gelatin silver bromo-chloride emulsions containing the adjuvant listed in the table below were made, coated, exposed and processed in the same manner as described in Example 2.

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0 |
| Methyldichlorosilane | 0.005 | 167 | 0 |

*Example 7*

A slow speed chlorobromide emulsion (AgCl=95.2 mol percent, AgBr=4.8 mol percent) was prepared by a formula which normally yields a satisfactory contact printing paper and was brought to optimum speed level preparatory to coating and additions of a sensitizing dye, glycerine, benzotriazole and chrome alum were made. To a portion of this emulsion was added a stabilized aqueous dispersion of silaceous particles of approximately 50 millimicrons diameter coated with 15–20% of hydrolyzed trichlorosilane $(HSiO_{1.5})_n$ where $n$ is 1 or greater in the quantity as shown per 1.5 mols silver halide. This emulsion was then coated on to a paper stock, dried and exposed in contact with a standard negative in a contact printer so that prints matched for photographic quality were obtained upon devolpment in the developer shown in Example 1 for 1.0 minute with the results tabulated below:

| Adjuvant | Grams | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0 |
| $SiO_2$ particles coated with hydrolyzed trichlorosilane | 2.20 | 163 | 0.02 |



*Example 8*

A high speed variable contrast enlarging silver bromo-iodide emulsion was prepared according to U. S. Patent 2,280,300, to a portion of which a stabilized aqueous dispersion of silica ($CiO_2$) particles control with 15–20% of hydrolyzed trichlorosilane $(HSiO_{1.5})_n$ was added immediately before digestion or after-ripening. The emulsion was then coated on a paper stock, finished and tested in accordance with the procedure given in Example 1. Exposures were made through both blue and green transmitting filters with serve to differentiate the varying contrast regions of spectral sensitivity of emulsions of this type. Results were as follows:

| Adjuvant | Gram per 1.5 mole silver halide | Relative Speed | | Fog |
|---|---|---|---|---|
| | | Blue Light | Green Light | |
| None | | 100 | 124 | 0 |
| $SiO_2$ particles coated with hydrolyzed trichlorosilane | 0.10 | 124 | 150 | 0.01 |

*Example 9*

A gelatino-silver halide emulsion containing about 93.5 mol percent of silver bromide and 6.5 mol percent of silver iodide was brought to its maximum light sensitivity and prepared for coating. Prior to digestion varying amounts based on 1.5 mol of silver halide of an aqueous dispersion of silaceous particles coated with hydrolized trichlorosilane were added to several separate portions of the emulsion as shown. The samples were coated on cellulose acetate film base and dried in the usual manner. The resulting coated elements were exposed to a series of graduated light intensities in an intensity scale sensitometer (Type 1–B) and then processed in a developer of the following composition:

| | Grams |
|---|---|
| N-methyl-para-aminophenol sulfate | 2.0 |
| Hydroquinone | 5.0 |
| Sodium sulfite | 98.0 |
| Borax | 2.0 |
| Water to make 1.0 liter | |

for 10 minutes at 68°, fixed, washed and dried. The following results were obtained at equal degrees of contrast:

| Total Weight Adjuvant Added-Grams | Relative Speed | Fog |
|---|---|---|
| None | 100 | 0.04 |
| 0.01 | 246 | 0.03 |
| 0.05 | 415 | 0.04 |

The silica particles of Examples 1, 2, 7, 8 and 9 had an average diameter of 0.015 micron and were obtained from Linde Air Products Company and those of Examples 3 and 4 had the same diameter but were obtained from Mallinckrodt Chemical Works under the trade name Si-O-Lite.

*Example 10*

A photographic emulsion comprising a dispersion of silver bromo-iodide in a hydrophilic hydrolyzed ethylene/vinylacetate copolymer of the type described in McQueen U. S. Patent 2,397,866 was prepared and during the final digestion was split into a number of portions. One of the portions was used as a control and digestion was continued. To the others were added the adjuvants listed in the following table. Digestion was continued and after addition of ammonium hydroxide and saponin, the various portions of emulsions were coated onto a paper base to form a thin layer and dried. Sample strips of the light-sensitive photographic papers were then exposed and processed in the manner described in Example 1 with the following results:

| Adjuvant | Grams per 1.5 mol silver halide | Relative Speed | Fog |
|---|---|---|---|
| None | | 100 | 0 |
| Cyclic $[C_2H_5(H)SiO]_4$ | 0.0025 | 2,540 | 0.15 |
| Methyldichlorosilane $(CH_3HSiCl_2)$ | 0.0025 | 1,940 | 0.05 |

The invention is, of course, not limited to the use of the specific silanic compounds mentioned in the foregoing examples nor to the specific amounts given in such examples. A large number of other silanic compounds which possess at least one silicon-hydrogen bond can be substituted in like manner.

The utility of any particular silanic compound which contains a silicon-hydrogen bond can be determined by testing whether it or its hydrolysis products are capable of exerting a reducing action on or nucleating silver halide. The mechanism or theory as to why the silanic compounds are effective as chemical sensitizers for silver halide emulsions is not completely understood but it is believed that the silicon-hydrogen linkage must be capable of alkaline induced hydrolysis which is illustrated in the following equation for a useful class of silanic compounds:

$$R_nSiH_{4-n} + HOH \xrightarrow{OH} R_nSiOH_{4-n} + H_2$$

where $R_n$ is hydrogen, halogen, e. g., Fl, Cl and Br; alkyl of 1 to 30 carbon atoms, alkoxy of 1 to 30 carbon atoms, aryl, e. g., phenyl, tolyl, naphthyl, etc.; aryloxy, e. g., phenoxy, naphthoxy, etc., siloxy or combinations thereof, $n$ being 1–3.

Among the additional suitable specific silanic compounds which can be used, there may be mentioned: alkyl silanes, e. g., methyl silane, dimethyl silane, trimethyl silane; ethyl silane, diethyl silane, triethyl silane, n-propyl silane, butyl silane; alkyl halogenosilanes, dimethylchlorosilane, ethyl dichlorosilane, diethylchlorosilane, propyl dichlorosilane; aryl silanes, e. g., diphenyl silane, triphenyl silane and mixed alkyl aryl silanes, e. g., ethyl diphenyl silane, methyl phenyl silane and dihexyl phenyl silane; alkoxy, aroxy, alkoxy halogeno, and aroxy halogeno silanes, e. g., diethoxy silane, methyl dichlorodiethoxy silane and phenoxy silane; cyclic and linear polymeric siloxanes, e. g., cyclic tetrameric methyl siloxane and its linear analogue $HO[CH_3(H)SiO]_4H$. Hydrolysis products of the above listed silanes which retain a silicon-hydrogen bond may also be used.

The invention is not limited to the use of one silanic compound as mixtures of two or more can often be used with satisfactory results. Nor is the invention limited to any particular method of application. When the silanic compounds are not used as coatings on inert particles they may be added to an aqueous colloid silver halide emulsion or an aqueous colloid solution as solutions in suitable solvents which do not have a deleterious effect on a light-sensitive silver halide. Among such solvents are methanol, ethanol, diethyl ether, acetone, benzene, etc.

The silanic compounds of the invention may be added to the hydrophilic or water-permeable colloid silver halide emulsions over a wide range of proportions, e. g., from 0.5 mg. to 370 mg. of said silanic compound per 1.5 mols of silver halide. The amount will, of course, vary with the particular silanic compound and the particular type of emulsion. They may be used with other emulsion sensitizers, e. g., sulfur sensitizers.

When the silanic compound is not added directly to the silver halide emulsion but is used in a continguous light-insensitive layer, e. g., a sub-layer or filter layer or overcoating they can be added to the coating solution, which is generally an aqueous solution or dispersion of a water-permeable colloid, e. g., gelatin, hydrolyzed ethylene/vinylacetate copolymers, polyvinyl alcohol, polyvinyl acetals including those which contain color forming nuclei such as those described in Jennings et al. U. S. Patent 2,397,864; polyglycuronic acids, hydrolyzed cellulose acetate, carboxymethyl cellulose, albumin, zein, casein, agar-agar, etc.

These colloids also have utility as binding agents for the silver halide grains in emulsion layers.

In order that the particles coated with such silanic compounds, may be dispersed rapidly and uniformly throughout the emulsions, it is desirable to use a wetting



or dispersing agent in an amount of 0.1 to 100% based on the total weight of the silanic compound-coated inert particle. Suitable agents include the oxyalkylene ethers of hexitol ring dehydration products, e. g., the polyoxyethylene sorbitan monolaurate, monostearate and monooleates which contain 2 to 20 oxyethylene groups divided in 3 chains. Additional specific agents of this type are described in Blake et al. U. S. Patent 2,400,532. Still other agents which may be suitable include octyl phenyl polyglycol ether; sodium lauryl sulfate and the dioctyl ester of sodium sulfosuccinic acid.

An advantage of this invention is that it provides silver halide emulsion layers which have enhanced photographic density and this can be attained in a simple and economical manner. A further advantage is that the silanic compounds are commercially available. Another advantage resides in the fact that the compounds in addition to conferring enhanced speed characteristics to the emulsions do not produce any material amount of fog. An advantage of the use of inert particles, e. g., silica particles, coated with the silanic compounds is that they do not migrate or diffuse in emulsion layers. This is of importance for uniformity and in multilayer photographic films and popers for color photography.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A photographic silver halide emulsion containing from 0.5 to 370 mg. of a silanic compound having at least one silicon-hydrogen bond per 1.5 mols of silver halide.

2. An emulsion as set forth in claim 1 wherein said compound is $CH_3HSiCl_2$.

3. A photographic gelatino-silver halide emulsion containing from 0.5 to 370 mg. of a silanic compound having at least one silicon-hydrogen bond per 1.5 mols of silver halide.

4. An emulsion as set forth in claim 3 wherein said compound is $[C_2H_5(H)SiO]_4$.

5. A photographic silver halide emulsion containing from 0.5 to 370 mg. of a silanic compound having at least one silicon-hydrogen bond per 1.5 mols of silver halide, said silanic compound being coated on the surface of inert particles having an average diameter from 0.001 to 10 microns.

6. An emulsion as set forth in claim 5 where said compound is a hydrolyzed trichlorosilane of the formula $(HSiO_{1.5})_n$ where $n$ is an integer of at least 1.

7. A photographic silver halide emulsion containing from 0.5 to 370 mg. of a silanic compound having at least one silicon-hydrogen bond per 1.5 mols of silver halide, said silanic compound being coated on the surface of silica particles having an average diameter from 0.001 to 10 microns.

8. An emulsion as set forth in claim 7 where said compound is $HO[(C_2H_5)HSiO]_nH$ where $n$ is 6 to 20.


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