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# PHOTOGRAPHIC SILVER HALIDE EMULSIONS CONTAINING A RUTHENIUM, PALLADIUM OR PLATINUM HYDROXIDE IN STABILIZING AMOUNTS AND PROCESS FOR PREPARING THE SAME

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This invention relates to photographic silver halide emulsions of improved stability and to a process of preparing the same. More particularly, it relates to such emulsions which contain water-insoluble hydroxides of ruthenium, palladium or platinum, and to a process of preparing the same.

Many compounds are known which have a good stabilizing or antifogging action in photographic silver halide emulsions. The utility of many of these compounds, however, is severely limited by their tendency to decrease the sensitivity of dispersions of light-sensitive silver halide in water-permeable colloids. Moreover, since the amount of the known stabilizing agents which can be added to a silver halide dispersion or emulsion without producing deleterious effects must be kept within a very narrow range of exceedingly low quantities, it is difficult to control the quality of the dispersions from batch to batch.

An object of this invention is to provide photographic silver halide emulsions of uniform quality and enhanced stability to aging, particularly with respect to aging under conditions of relatively high humidity and at elevated temperatures, e.g., tropical conditions. Another object is to provide such emulsions which are optically sensitized. A further object is to provide a process for increasing the stability of photographic silver halide emulsions, especially high-speed silver iodobromide emulsions, optically sensitized and not, without adversely affecting the sensitivity of the freshly prepared or coated emulsions. A still further object is to provide such a process while simultaneously reducing the degree of fog produced upon aging and without adversely affecting the sensitivity of the aged emulsion layers of photographic films and papers. A still further object is to provide such process wherein the amount of stabilizing agent added does not have to be maintained within a narrow range. Still further objects will be apparent from the following description of the invention.

The foregoing objects are attained and stable photographic silver halide emulsions and emulsion layers provided in accordance with the invention by adding to an aqueous light-sensitive silver halide emulsion a small amount of at least one water-insoluble metal hydroxide of a metal taken from the group consisting of ruthenium, palladium and platinum, wherein these metals have their principal valencies.

The above metal hydroxides preferably are added to the emulsion after the completion of the digestion stage where the emulsion is brought to its optimum sensitivity prior to coating. Various emulsion adjuvants can be added to the digested emulsion, prior to, simultaneously with, or even subsequent to the addition of the water-insoluble heavy metal hydroxide. Among such adjuvants are spreading agents, anti-foaming agents, sulfur sensitizers, e.g., sodium thiosulfate, thiourea, allyl thiourea and allyl thiocarbamide, and sensitizing amounts of polyoxyalkylene compounds containing at least six oxyalkylene groups of 2 to 3 carbon atoms.



The emulsion sensitizing agents of the polyoxyalkylene type can be present in the emulsions in the usual sensitizing amounts. The useful agents of this type include (*a*) various polyoxyalkylene glycols and derivatives thereof, e.g., alkyl ethers, fatty acid esters and (*b*) condensation products of hexitol ring dehydration products with ethylene oxide or propylene oxide containing at least six oxyalkylene groups, having a molecular weight, or an average molecular weight of at least 400 to about 8000 or more. Suitable compounds of these types are disclosed in U.S. Patents 2,423,549, 2,441,389, 2,240,472, 1,970578 and 2,400,532.

In preparing the stabilized emulsions of the invention, the water-insoluble heavy metal hydroxide is used in very fine particle size, e.g., from 2 to 50 and preferably 2 to 10 microns, and is preferably added from aqueous dispersion. The dispersion or suspension can be easily prepared from the pure metal hydroxide.

As an exemplary procedure, a suspension of these materials is prepared by first weighing out 5.0 grams of the metal hydroxide and adding to this amount about 20 grams of glass beads. To this mixture there is added 20 ml. of distilled water. The mixture is placed in a ball mill and mixed for 48 hours. The glass beads are then removed and the suspension diluted with distilled water to a convenient concentration, usually about .01 gram of the metal hydroxide per 1000 ml. of distilled water. The procedure for preparation is the same for each of the metal hydroxides.

The optimum amount of the metal hydroxide stabilizer may vary for a given emulsion depending on the presence of emulsion adjuvants such as chemical sensitizers, optical sensitizers, etc. We have found that the amount to be added should be less than 0.1 mole of the metal hydroxide per 1000 moles of silver halide. The preferred ranges are 0.0095 to 0.95 mole of palladium hydroxide and 0.0087 to 0.087 mole of ruthenium hydroxide per 1000 moles of silver halide. In the case of platinum hydroxide, it preferably should be kept below 0.0063 mole and above 0.0025 mole per 1000 moles of silver halide.

The invention is useful in stabilizing various types of silver halide emulsions including silver chloride, silver bromide, silver chlorobromide and silver chloroiodobromide emulsions of pH 5.0 to 8.0 and greater, and emulsions made by admixing two or more of the foregoing silver halides. In the preferred aspect of the invention, an aqueous suspension of the finely divided metal hydroxide is thoroughly admixed with an aqueous gelatin high-speed silver iodobromide emulsion containing naturally occurring sulfur sensitizers. Silver halide emulsions containing other types of water-permeable colloid binding agents having protective colloid properties, particularly those of the reversible type, can be treated in accordance with the invention. Among such binding agents are natural and synthetic colloids, e.g., albumin, casein, agar-agar and polyvinyl alcohol and its partial ethers, esters and acetals.

The following examples will further illustrate but are not intended to limit this invention and in the tables the amount of metal hydroxide is in parts of grams or grams per mole of silver halide, which is referred to as AgX. In these examples, the emulsions are prepared and coated in the absence of actinic radiations in amounts which would cause a significant exposure of the emulsions.

*Example I*

A high-speed gelatino-silver iodobromide emulsion of the X-ray type containing approximately 1.5 mole percent silver iodide and 98.5 mole percent silver bromide is prepared in the conventional manner. The emulsion is divided into two equal parts which are given a normal

digestion. One digested part, without further treatment, is coated onto a cellulose acetate film base. To the other part, palladium hydroxide, $Pd(OH)_2$, in the amount shown in the following table, is added. Samples of the film elements were then given an X-ray screen exposure of 15 milliampere-seconds, 71 kilovolts potential, at a distance of 55 inches through a 1 millimeter aluminum filter using an aluminum step wedge and then were developed in a developer of the following composition:

| | Grams |
|---|---|
| N-methyl p-aminophenol hydrosulfate | 3.0 |
| Hydroquinone | 9.0 |
| Sodium sulfite (desiccated) | 50.0 |
| Potassium bromide | 4.5 |
| Potassium carbonate | 50.0 |

Add water to make 1.0 filter.

for 5 minutes at 68° F. with the results shown in the following table:

| $Pd(OH)_2$ | Speed | Fresh Contrast | Fog | 7 days–120° F.–65% R.H. | | |
|---|---|---|---|---|---|---|
| | | | | Speed | Contrast | Fog |
| None | 1,000 | 3.24 | .03 | 990 | 2.30 | .11 |
| 0.0133 | 1,060 | 3.27 | .03 | 990 | 2.40 | .07 |

*Example II*

Example I is repeated except that the emulsion is divided into four parts which are digested, and ruthenium hydroxide, $Ru(OH)_3$, is added in the amounts shown in the following table to three parts in place of the palladium hydroxide. The film elements were exposed and developed as described in Example I with the results listed in the following table:

| $Ru(OH)_3$ | Speed | Fresh Contrast | Fog | 7 days–120° F.–65% R.H. | | |
|---|---|---|---|---|---|---|
| | | | | Speed | Contrast | Fog |
| None | 1,000 | 2.94 | .06 | 880 | 2.39 | .14 |
| .0067 | 950 | 3.14 | .05 | 870 | 2.46 | .09 |
| .0013 | 990 | 2.99 | .05 | 880 | 2.36 | .12 |
| .0133 | 970 | 2.96 | .04 | 860 | 2.32 | .12 |

*Example III*

Example I is repeated except that the emulsion is divided into four parts which are digested and platinum hydroxide, $Pt(OH)_2 \cdot 2H_2O$, in the amount shown in the following table, is added to three parts in place of the palladium hydroxide. The film elements were exposed and developed as described in Example I with the results listed in the following table:

| $Pt(OH)_2 \cdot 2H_2O$ | Speed | Fresh Contrast | Fog | 7 days–120° F.–65% R.H. | | |
|---|---|---|---|---|---|---|
| | | | | Speed | Contrast | Fog |
| None | 1,000 | 3.03 | .06 | 930 | 2.31 | .26 |
| .00067 | 1,000 | 2.99 | .06 | 950 | 2.63 | .14 |
| .00167 | 980 | 3.05 | .05 | 900 | 2.76 | .07 |
| .00133 | 920 | 3.09 | .04 | 880 | 2.54 | .06 |

*Example IV*

Example I is repeated except the emulsion is divided into four equal parts and $Pd(OH)_2$, in the amounts shown in the following table, is added to three portions in lieu of the amounts indicated in Example I. The film elements were exposed and developed as described in Example I with the results listed in the following table:

| $Pd(OH)_2$ | Speed | Fresh Contrast | Fog | 7 days–120° F.–65% R.H. | | |
|---|---|---|---|---|---|---|
| | | | | Speed | Contrast | Fog |
| None | 1,000 | 3.24 | .03 | 840 | 1.62 | .33 |
| .0013 | 1,000 | 2.94 | .04 | 890 | 2.17 | .20 |
| .0033 | 1,000 | 2.95 | .05 | 860 | 2.24 | .15 |
| .0133 | 1,000 | 2.91 | .06 | 840 | 2.24 | .17 |

It will be apparent from the foregoing examples that the stability of photographic silver halide emulsions is markedly improved, particularly with regard to fogging at elevated temperatures.

Various salts and complexes of noble metals including those of the above metals have been added to photographic silver halide emulsions for toning, sensitizing and other purposes. Insofar as applicant is aware these salts and complexes have been of the water-soluble type. Palladium chloride and nitrate, for example, when used in stabilizing amounts, desensitize a silver halide emulsion. Platinum complexes have a desensitizing effect on silver halide emulsions. Platinum chloride has no appreciable effect as a sensitizer.

An advantage of the invention resides in the fact that the metal hydroxides used, being insoluble, do not have a localized reaction at the point where the stabilizer is introduced into the emulsion. Ions are released more slowly, and this leads to more uniformly stabilized emulsions than it has been possible to obtain by means of water-soluble metal compounds.

An advantage of this invention is that it provides a simple and effective process for improving the stability of photographic emulsions. The process is not only simple but it uses chemical compounds which are easily prepared. Another advantage is that the process of stabilizing the emulsions can be practiced successfully by the ordinary technician, and extreme care does not have to be exercised in the amount of metal hydroxide added since a relatively large amount still contributes stabilizing properties to the emulsion. Stabilization of the freshly prepared and coated emulsions, moreover, is accomplished without adverse effects on the optimum sensitivity of the freshly prepared emulsions. The emulsions have high initial speed and good stability, that is, have relatively low fog values initially and upon aging.

I claim:

1. A process for the stabilization of a digested photographic water-permeable colloid-silver halide emulsion which comprises uniformly admixing with said emulsion an aqeuous dispersion of finely divided particles of a water-insoluble metal hydroxide taken from the group consisting of ruthenium, palladium and platinum hydroxide in a stabilizing amount less than 0.1 mole per 1000 moles of silver halide.

2. A process as set forth in claim 1 wherein said colloid is gelatin.

3. A process as set forth in claim 1 wherein said hydroxide has a particle size of not more than 50 microns in average diameter.

4. A process as set forth in claim 1 wherein said emulsion is a high-speed silver iodobromide emulsion.

5. A water-permeable colloid silver halide photographic emulsion having uniformly admixed therethrough a stabilizing amount of at least one water-insoluble metal hydroxide taken from the group consisting of ruthenium, palladium and platinum hydroxide which is present in an amount above 0.0025 and less than 0.1 mole per 1000 moles of silver halide.

6. A photographic emulsion as set forth in claim 5 wherein said hydroxide is present in the form of particles having an average diameter less than 50 microns.

7. A photographic emulsion as set forth in claim 5 wherein said colloid is gelatin.

8. A photographic element comprising a sheet support bearing at least one layer of a water-permeable colloid silver halide photographic emulsion having uniformly admixed therethrough a stabilizing amount of at least one water-insoluble metal hydroxide taken from the group consisting of ruthenium, palladium and platinum hydroxide which is present in an amount above .0025 and less than 0.1 mole per 1000 moles of silver halide.

9. An element as set forth in claim 8 wherein said support is a hydrophobic film base.



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