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CHEMICAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

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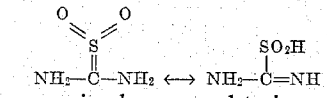
This invention relates to photographic silver halide emulsions, and more particularly, to a means for chemically sensitizing such photographic silver halide emulsions.

A number of methods have been previously proposed for increasing the sensitivity of photographic silver halide emulsions, other than methods of optical or spectral sensitization which involve the incorporation of certain dyes in the emulsions. The incorporation of dyes in the emulsions increases the optical range of sensitivity, whereas the incorporation of other materials known as chemical sensitizers increases the speed and generally the gamma of the emulsion without materially affecting the optical range of sensitivity. Many of the prior methods of enhancing sensitivity, other than the methods of spectral sensitization, leave much to be desired because the increase of sensitivity may be quite small or the increase in sensitivity is accompanied by excessive fog and/or excessively poor keeping qualities of the sensitized emulsions.

We have now found a method of increasing the sensitivity of photographic silver halide emulsions wherein the speed increases are quite substantial, while the fog and keeping qualities are not excessively affected, considering the magnitude of the increases in speed and gamma or contrast obtained.

It is, therefore, an object of our invention to provide photographic silver halide emulsions which have been chemically sensitized. Another object is to provide a method of preparing such sensitized emulsions. Still another object of our invention is to provide photographic silver halide emulsions which have increased sensitivity, without concomitant increases in fog, or poor keeping qualities, to a degree which might seriously affect the usefulness of the sensitized emulsions. Other objects will become apparent from a consideration of the following description and examples.

According to our invention, we have found that the sensitivity of photographic silver halide emulsions can be materially increased by incorporating formamidine sulfinic acid therein. Formamidine sulfinic acid is sometimes known as thiourea dioxide, depending upon the particular tautomeric form in which the compound is written. Formamidine sulfinic acid (or thiourea dioxide) can be represented as existing in the following state of equilibrium:



It has been previously proposed to incorporate various sulfinic acids in photographic silver halide emulsions for the purpose of increasing the stability thereof. For example, U.S. Patent 2,057,764 suggests the addition of alkane sulfinic acids, such as methane sulfinic acid, ethane sulfinic acid, etc., to photographic silver halide emulsions for the purpose of stabilization. However, as noted in this patent, these sulfinic acids have no detectable effect upon the sensitivity characteristics of the photographic silver halide emulsions. Contrasted with this behavior, the formamidine sulfinic acid of our invention has a profound effect upon the sensitivity characteristics of the photographic silver halide emulsions. Moreover, we have found that even more closely related acids than

the sulfinic acids of U.S. Patent 2,057,764 fail to effectively increase the sensitivity of photographic silver halide emulsions. For example, various types of substitution on the nitrogen atom or atoms of formamidine sulfinic acid appears to materially decrease or destroy the sensitizing characteristics of the parent compound.

The preparation of silver halide emulsions involves three separate operations: (1) the emulsification and digestion or ripening of the silver halide, (2) the freeing of the emulsion from excess soluble salts, usually by washing, and (3) the second digestion or after-ripening to obtain increased sensitivity. (Mees, "The Theory of the Photographic Process," 1942). We prefer to add the sensitizing compound of our invention before the final digestion or after-ripening, although it can also be added after digestion.

The quantity of formamidine sulfinic acid added to the photographic silver halide emulsions can be varied, depending upon the particular effect desired, degree of ripening, silver halide content of the emulsion, etc. We have found that generally from about 0.05 to about 20 mg. of formamidine sulfinic acid per mole of silver halide is quite satisfactory to accomplish the sensitization of the emulsions. We have further found that increased sensitization can be obtained, and that larger quantities of formamidine sulfinic acid can be employed, in cases where the final ripening of the silver halide emulsion is carried out for longer periods of time than normal, but at lower ripening temperatures.

The photographic silver halide emulsions used in practicing our invention are generally of the developing-out type. It is to be understood that the amount of silver halide in the emulsions can be varied, depending upon the particular purpose for which the emulsion is to be employed. Particularly useful results can be obtained when formamidine sulfinic acid is employed in conjunction with gelatino-silver-bromiodide emulsions, although it can also be advantageously employed in sensitizing other silver halide emulsions, such as gelatino-silver-chloride, -bromide, -chlorobromide, -chlorobromiodide, etc., emulsions.

The photographic silver halide emulsions used in practicing our invention can also be optically sensitized by means of the dyes customarily employed in photography, such as cyanine dyes, carbocyanine dyes, dicarbocyanine dyes, merocyanine dyes, holopolar dyes, etc. The sensitizing effect obtained in our invention is not completely independent of the optical or spectral sensitizing dyes commonly used, although no adverse effects have been noted in using emulsions which have been optically sensitized. Also, the formamidine sulfinic acid of our invention can be employed in conjunction with other chemical sensitizers.

The photographic silver halide emulsions employed in practicing our invention can also contain antifoggants or materials known to stabilize the emulsions against loss of speed under adverse keeping conditions, such as those customarily encountered in the tropics. Such antifoggants include, for example, those described in Allen et al. U.S. application Serial No. 586,654, filed May 23, 1956, as well as many of the antifoggant compounds which can be generally classed as polyazaindenes. Such polyazaindenes have been described in U.S. Patents 2,444-604–9; 2,743,181; 2,735,769; etc.

The photographic silver halide emulsions employed in our invention can be used in the preparation of materials, such as multilayer materials, intended for use in color photography, where a number of separate silver halide emulsion layers are sensitized for a particular region of the spectrum. Such multilayer color materials generally have a red-sensitive layer coated on a support, followed by a green-sensitive layer, a blue light-absorb-

ing layer, and a blue-sensitive layer, together with one or more interlayers comprising gelatin or some other colloid having various addenda, such as ultraviolet absorbing agents, etc., incorporated therein. These light-sensitive layers can contain color-forming materials of the type customarily employed in color photography, such as coupling compounds containing reactive ketomethylene groups, phenolic groups, or heterocyclic groups, such as pyrazolone. See, for example, U.S. Patent 2,640,776. These color-forming compounds can be incorporated in water-insoluble, low molecular weight, organic, crystalloidal materials having a boiling point above about 175° C., such materials being of the type described in U.S. Patent 2,322,027.

It has been found that the chemical sensitizer of our invention is useful in combination with emulsions which have been sensitized with gold salts, such as those described in Waller and Dodd U.S. Patent 2,399,038, or Damschroder U.S. Patent 2,597,856 or Yutzy and Leermakers U.S. Patent 2,597,915 (e.g., potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride, 2-aurosulfobenzothiazole methochloride, etc.). Also, emulsions which have been sulfur-sensitized, such as by the procedures shown in Sheppard U.S. Patent 1,574,944 or U.S. Patent 1,623,499 or Sheppard and Brigham U.S. Patent 2,410,689 can be employed in our invention. Such sulfur-sensitized emulsions can additionally contain gold sensitizers of the type mentioned above, or gold compounds intended primarily for stabilization purposes.

The following examples will serve to illustrate more fully the manner of practicing our invention:

Example 1

A fine-grain, low-gelatin, positive speed bromiodide emulsion was prepared and washed by the acid coagulation method described in U.S. Patent 2,614,928. The pH of the emulsion was then adjusted to 6.0 and the emulsion held for 50 minutes at 60° C., both in the absence and presence of formamidine sulfinic acid. Additional gelatin and a coating aid, such as saponin, were then added and the emulsion coated on a suitable support, such as glass, cellulose acetate film, polyvinyl resin film, etc. After drying, the coatings were exposed for 1/25 second positive on an Eastman Type Ib sensitometer and developed for 6 minutes at 70° F. in a developer having the following composition:

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N-methyl-p-aminophenol sulfate	0.3
Hydroquinone	6.0
Sodium sulfite (dry)	38.0
Sodium bisulfite	1.5
Sodium carbonate monohydrate	22.0
Sodium bromide	0.78
Citric acid	0.7

Water to make one liter.

The speed contrast and fog for each of the emulsion coatings was measured, comparison being made between the coating containing no formamidine sulfinic acid, and coatings containing formamidine sulfinic acid in the quantities indicated below (the amount being on the basis of per mole of silver halide present). The results follow:

Coating	Formamidine sulfinic acid (mg./mole AgX)	30/E Speed	Gamma	Fog
(a)	None	1.20	0.36	.05
(b)	0.5	4.10	1.28	.05
(c)	1.5	5.25	1.33	.05

Example 2

A fine-grain emulsion prepared in exactly the manner shown in Example 1, except that the final digestion was for 1 hour at 40° C., was treated in the presence and absence of formamidine sulfinic acid in the amounts indicated below. Speed, gamma and fog of each of the resulting coatings were measured as in Example 1. The results follow:

Coating	Formamidine sulfinic acid (mg./mole AgX)	30/E Speed	Gamma	Fog
(a)	None	1.90	0.46	.04
(b)	5.0	4.80	1.28	.05
(c)	10.0	6.60	1.36	.04

Example 3

A fine-grain photographic emulsion was prepared according to the method described in Example 2, except that the emulsion was then sulfur-sensitized, for example, as described in U.S. Patent 1,574,944. A batch of this emulsion containing no formamidine sulfinic acid sensitizer was then compared with an identical batch containing the sensitizer in the amounts indicated below. Exposure and development was identical to that of Example 1. The results follow:

Coating	Formamidine sulfinic acid (mg./mole AgX)	30/E Speed	Gamma	Fog
(a)	None	22.80	3.02	.05
(b)	5.0	52.5	3.80	.06

When employing the formamidine sulfinic acid of our invention in alkaline photographic silver halide emulsions, it is to be understood that an alkali metal salt thereof may be formed and that the alkali metal salt exists in ionic form. The probability of salt formation under such alkaline conditions is well understood by those skilled in the art and it is to be understood that the reference in the foregoing specification, and in the following claims, to formamidine sulfinic acid includes the use of such material in acid or alkaline emulsions. As indicated above, these photographic emulsions can be sensitized or not, by means of optical sensitizing dyes. Such photographic emulsions can be orthochromatic, panchromatic, or X-ray emulsions. If used with spectral sensitizing dyes, the formamidine sulfinic acid can be added to the emulsion before or after such dyes are added. Suitable dispersing agents for the silver halide emulsions sensitized according to our invention comprise gelatin, or other colloids, such as collodion, albumen, cellulose organic derivatives, synthetic resins, etc.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. An unexposed photographic silver halide emulsion containing a sensitizing amount of formamidine sulfinic acid.

2. An unexposed photographic gelatino-silver-halide developing-out emulsion containing a sensitizing amount of formamidine sulfinic acid.

3. An unexposed photographic gelatino-silver-bromiodide developing-out emulsion containing a sensitizing amount of formamidine sulfinic acid.

4. An unexposed photographic silver halide emulsion containing a sensitizing amount of formamidine sulfinic acid and a sulfur-sensitizer.

5. An unexposed gold-sensitized photographic silver halide emulsion containing a sensitizing amount of formamidine sulfinic acid.

6. An unexposed acid photographic silver halide emulsion containing a sensitizing amount of formamidine sulfinic acid.

References Cited in the file of this patent

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