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2,441,440

SILVER HALIDE PHOTOGRAPHIC EMULSIONS OF ENHANCED LIGHT SENSITIVITY

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This invention pertains to photographic emulsions and more particularly to colloid-silver halide emulsions of enhanced light-sensitivity. Still more particularly it pertains to gelatino-silver halide emulsions of enhanced light-sensitivity and to processes of preparing such emulsions.

A large amount of research work has been done on increasing the light-sensitivity of photographic emulsions. The most practical compounds for this purpose contain a divalent sulfur compound. Representative compounds of this type are described in United States Patent 1,623,449. Other useful compounds include aldehydes such as formaldehyde, alkaline hypophosphites, hydroxylamine and substituted hydroxylamines. There is no criterion however by which one can predict the utility of a chemical compound with certainty in advance of actual experimentation. The art is still highly empirical.

An object of this invention is to provide new means for increasing the light-sensitivity of colloid-silver halide emulsions. Another object is to provide gelatino-silver halide emulsions of enhanced light-sensitivity utilizing available chemical compounds. A related object is to provide such emulsions using economical chemicals. A further object is to increase the light-sensitivity of emulsions by a simple and economical method. A still further object is to provide a method of preparing gelatino-silver halide emulsions of increased light-sensitivity which does not have a deleterious effect on the spectral sensitivity of such emulsions. Still other objects will be apparent from the following description of the invention.

It has been discovered that colloid-silver halide emulsions of increased sensitivity may be made by incorporating therewith the condensation products of aliphatic aldehydes with ammonia or an amine. These condensation products may be incorporated with the emulsion at any time during their preparation but are preferably added after the initial preparation of the emulsions but before digestion has been completed.

In the case of gelatino-silver halide emulsions it has been found that the addition of the condensation products of aliphatic aldehydes with ammonia or aliphatic or aromatic amines to such compositions, results in emulsions of decidedly improved light-sensitivity without imparting any undesirable fog characteristics thereto.

It has been further discovered that the sensitivity of the emulsions depends upon the specific nature of the condensation products described

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above. Freshly prepared condensation products, for instance, confer less light-sensitivity to an emulsion than aged condensation products. Ageing can be accelerated by heating to an elevated temperature. The color of the products likewise change on ageing. Acetaldehyde-ammonia condensation products, for example, when freshly prepared are white crystals. On standing at room temperature for several weeks they change to a yellow or a yellow-red color. The lighter colored products can be rapidly changed by heating at an elevated temperature, below the melting point of the crystals for a short period. The darker colored products, in general, give better results than the white colored products. Hence, the activity of the condensation products can be correlated roughly with their color.

The sensitization conferred to the final colloid silver halide emulsions is of the optical type and gives them an overall increase in speed, as distinguished from the extra range of spectral sensitivity conferred by sensitizing dyes. The condensation products can advantageously be used in conjunction with spectral sensitizing dyes, thereby modifying the normal spectral sensitivity and speed of emulsions.

The reasons the aldehyde-ammonia or aldehyde-amine complexes increase the sensitivity is not fully understood. It is due to the chemical nature of the complexes or condensation products, because the use of the individual components separately or in admixture with each other in a single emulsion produce no comparable sensitization.

There are obviously various ways of bringing the condensation products into operative contact with the silver salts and colloid binding agents. The condensation products may be incorporated in the emulsion at practically any stage in its manufacture and can even be associated therewith after coating to form light-sensitive layers. Thus, the silver halide emulsion layers can be impregnated with an aqueous solution or a dilute methanol or ethanol solution of the condensation products. Another manner consists in incorporating them in a hydrophilic colloid solution, e. g., aqueous gelatin and coating the admixture onto a gelatin-silver halide layer.

The following examples further illustrate the invention. The parts are by weight.

Example 1

Gelatino-silver iodobromide emulsions were prepared containing 0, 18.75, and 37.50 milligrams of an acetaldehyde-ammonia condensation prod-

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uct having a melting range of about 70 to 80° C. and being yellow-colored crystals, per 1.5 moles of silver halide. The emulsions were then given a first digestion, washed, given a second digestion, brought to their maximum light sensitivity and coated onto a suitable support. The following effects on relative speed were obtained.

	Mgs. Acetaldehyde-ammonia Present	Relative Speed
1	0	100
2	18.75	106
3	37.50	125

Example 2

Several amounts of n-propanal-ammonia condensation product having a boiling point of about 75° C. at 12 mm. pressure and being a yellow colored liquid ranging from 0 to 150 mg. were added separately to photographic gelatin silver halide emulsions each containing 1.5 mols of silver halide. The additions were made before the final digestion process, and the emulsions were then brought to their maximum light-sensitivity and coated onto a suitable support. The following results were obtained.

	Mgs. Propanal-ammonia	Relative Speed
1	0	100
2	25	105
3	50	113
4	75	129
5	112.5	137
6	150	157

Example 3

A photographic gelatin silver halide emulsion was panchromatized by the addition of a suitable cyanine dye and brought to its maximum light sensitivity. This emulsion was split into four equal parts before coating and from 0 to 333.3 mg. of the acetaldehyde-ammonia condensation product described in Example 1 was added per 1.5 mols of silver halide. Evaluation of the coated emulsions showed the following characteristics.

	Mgs. Acetaldehyde-ammonia	Relative Speed
1	0	100
2	83.3	140
3	166.6	170
4	333.3	170

Example 4

To an orthochromatized photographic gelatin silver halide emulsion, containing 1.5 mols of silver halide, was added from 0 to 7.5 mg. ethylidene aniline (an acetaldehyde-aniline condensation product described in U. S. Patent 1,658,220) before the second digestion period. Effects are tabulated below.

	Mgs. Ethylidene Aniline	Relative Speed
1	0	100
2	3.75	130
3	7.50	160

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Example 5

A photographic gelatin silver halide emulsion coated on a support was over-coated with layers containing an acetaldehyde-ammonia complex of the type given in Example 1 in concentrations equivalent to from 0 to 25 mg. per 1.5 mols of silver halide. The relative effects on the sensitivity of the emulsions are shown as follows:

	Mgs. Acetaldehyde-ammonia	Relative Speed
1	0	100
2	12.5	113
3	25	118

Example 6

To photosensitive gelatin silver halide emulsions, each containing 1.5 mols of admixed silver bromide and silver iodide, was added from 0 to 15 mgs. of a crotonaldehyde ammonia condensation product, being a yellow, amorphous solid having a melting range of 43 to 70° C. The emulsions were held at 120° F. for 60 minutes, coated on a suitable support, and the speeds were later determined. The effect on the speed of the emulsion is tabulated below.

	Mgs. Crotonaldehyde ammonia	Relative Speed
1	0	100
2	7.5	128
3	15	141

Example 7

Selected concentrations from 0 to 30 mgs. of a crotonaldehyde-aniline condensation product (a yellow-amber colored liquid which is described in U. S. Patents 1,417,970; 1,780,326 and 1,780,334) were added separately to gelatin silver halide emulsions containing 1.5 mols of silver salts to produce the following speed increases.

	Mgs. Crotonaldehyde aniline	Relative Speed
1	0	100
2	15	107
3	22.5	110
4	30	128

Example 8

An acetaldehyde - p - toluidine - aniline (described in U. S. Patent 1,638,220) condensation product in amounts ranging from 0 to 12.5 mgs. was added to photographic emulsions each containing 1.5 mols of silver halide. The following results were obtained.

	Mgs. Acetaldehyde-p-toluidine aniline	Relative Speed
1	0	100
2	9.25	114
3	12.50	129

Example 9

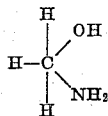
From 0 to 5 mgs. of n-butyraldehyde-n-butylamine condensation product (a translucent amber

Liquid described in U. S. Patents 1,417,970; 1,780,326 and 1,780,334, when added to photographic gelatin emulsions each containing 1.5 mols of silver halide produced the following effects.

	Mgs. Butyraldehyde-butylamine	Relative Speed
1	0	100
2	2.5	114
3	5	122

In place of the specific aldehyde-ammonia or aldehyde amine condensation products described in the above examples, there may be substituted other such condensation products. One or more of them can be used in an emulsion. Thus the condensation products of formaldehyde, acetaldehyde, n-propionaldehyde, butyraldehyde, secondary butyraldehyde, crotonaldehyde, etc. with ammonia, methylamine, ethylamine, n-butylamine, etc.; aniline, ortho, meta and paratoluidine, alpha and beta naphthylamine, and para phenylenediamine are useful.

The actual structural configuration of the organic molecules of the condensation products and particularly those which have been heat treated or aged at elevated temperatures is not known with certainty. The acetaldehyde-ammonia is believed to first form an addition complex product which has the structural formula:



This is not a very stable configuration, however, and secondary reactions lead to condensation products which are more complex structures. To illustrate this aldehyde-ammonia was prepared by passing ammonia gas into an ether solution of acetaldehyde at temperatures of -33°C , 0°C , and 20°C . The reaction products were separated and one portion of each was subjected to a heat treatment which consisted of holding for 48 hours at 65 to 70°C . When resulting products were tested photographically the following data were obtained.

Temperature of Preparation	Heat Treatment	Conc., mgs. per 1.5 mols AgBr	Relative Speed	Fog
Control		0	81	.07
-33°C	No ¹	37.5	81	.02
-33°C	No ¹	56.3	79	.05
-33°C	Yes	3.75	117	.05
-33°C	Yes	7.5	135	.06
0°C	No	37.5	87	.04
0°C	No	56.3	89	.03
0°C	Yes	3.75	129	.05
0°C	Yes	7.5	141	.11
20°C	No	37.5	107	.02
20°C	No	56.3	112	.02
20°C	Yes	3.75	117	.04
20°C	Yes	7.5	135	.07

¹ This product was a white crystalline addition compound made from 1 mol of acetaldehyde and 1 mol of ammonia.

It will be noted that the products increase in activity with increased temperature of preparation. Products made and kept at very low temperatures, e. g., -33°C . show little if any activity. The products made at such low temperatures when heated, however, become active. The maximum activity of the products is obtained by heat treatments of less than 48 hours at 65 to 70°C .

Beyond this period no significant increase in activity occurs.

Many useful aldehyde-ammonia complexes are well known and available compounds. Among the useful ones are those described in U. S. Patents 1,417,970; 1,418,824; 1,571,739; 1,638,220; 1,780,326 and 1,780,334.

The aldehyde-ammonia or amine complexes may be used in conjunction with known sensitizers such as allyl thiourea, phenyl isothiocyanate, sodium thiosulfate, and alkali metal hypophosphites.

They may also be used in conjunction with fog inhibiting agents, emulsion stabilizers and spectral sensitizing dyes such as cyanine, carbocyanine, merocyanine, cyazine, neocyanine, pseudocyanine, hemicyanine and styryl dyes; color formers and other emulsion constituents.

Amounts of 1 to 250 milligrams of the condensation products per mol of silver halide represents a practical range and 5 to 50 mg. per mol a preferred range. However, depending on the initial activity of the condensation product, amounts representing 5- to 10-fold increases, or more, over the maximum amounts described herein, can be employed in the present process.

Colloid binding agents other than gelatin may be used in the emulsions and emulsion layers. Collodion, agar-agar, albumin, polyglycuronic acid, hydrophilic cellulose derivatives and vinyl alcohol polymers and interpolymers and polyamides for instance can be substituted in whole or in part for the gelatin of the emulsions set forth in the above examples.

Simple and mixed silver halide emulsions, e. g., silver chloride, silver bromide, silver-chloride bromide, silver bromide iodide, silver chloride iodide, etc. are benefited by the addition of the novel aldehydic products described in this specification.

The invention has many advantages. It provides stable emulsions of enhanced light sensitivity. Substantial increases in emulsion speeds can be attained without any material increase in fog. The process is simple and does not require any new or additional equipment to the photographic manufacturer.

Aldehyde-ammonia or -amine addition products which apparently are first formed by the interaction of these components, especially at low temperatures, can be added to the emulsions if desired in place of the condensation products. The addition products upon aging of the emulsions are converted to condensation products which exhibit the beneficial results described above. This conversion is accelerated by an increase in temperature.

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.

We claim:

1. A colloid silver halide emulsion containing from 1 to 250 milligrams per mol of silver halide of a condensation product of an aliphatic aldehyde with a base taken from the group consisting of ammonia and primary amines.
2. A gelatino-silver halide emulsion containing from 1 to 250 milligrams per mol of silver halide of a condensation product of an aliphatic aldehyde with a base taken from the group consisting of ammonia and primary amines.
3. A colloid silver halide emulsion containing from 5 to 50 milligrams per mol of silver halide

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of a condensation product of an aliphatic aldehyde with a base taken from the group consisting of ammonia and primary amines.

4. A gelatino-silver halide emulsion containing from 5 to 50 milligrams per mol of silver halide of a condensation product of an aliphatic aldehyde with a base taken from the group consisting of ammonia and primary amines.

5. A gelatino-silver halide emulsion containing from 1 to 250 milligrams per mol of silver halide of a condensation product of a saturated aliphatic aldehyde of 1 to 4 carbon atoms with a primary aromatic amine.

6. A gelatino-silver halide emulsion containing from 5 to 50 milligrams per mol of silver halide of a condensation product of a saturated aliphatic aldehyde of 1 to 4 carbon atoms with a primary aromatic amine.

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7. A gelatino-silver halide emulsion containing 5 to 50 milligrams per mol of silver halide of a condensation product of acetaldehyde with ammonia.

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