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PHOTOGRAPHIC SILVER HALIDE EMULSION STABILIZED WITH ETHYLENE-DIUREA

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ABSTRACT OF THE DISCLOSURE

A stabilized silver halide photographic emulsion which is sensitized with alkylene oxide polymers and stabilized with ethylene-diurea.

The instant invention is directed to photographic emulsions and in particular, to light-sensitive silver halide emulsions which are sensitized with alkylene oxide polymers and which contain therein as a stabilizing agent ethylene-diurea.

In the past the sensitivity of photographic emulsions, i.e. light-sensitive gelatino silver halide emulsions, has been increased by the incorporation therein of various alkylene oxide polymers. The sensitizing additives employed have been compounds such as polyoxyalkylene ethers of hexatans or hexides which have at least one hydroxyl group replaced by a polyoxyalkylene radical, and which have also contained at least one lipophilic radical such as a long chain aliphatic hydrocarbon radical or a long chain aliphatic monocarboxylic ester. Compounds of this type have been incorporated into the emulsion, both prior to coating or subsequent thereto.

Furthermore, the sensitizing agents have been incorporated in a substratum coating or in an over coating which is placed in intimate contact with the emulsion layer.

In addition to the above sensitizing agents, polyalkylene glycols and in particular, higher poly glycols which have a molecular weight in excess of 400 have also been incorporated as sensitizing or speed enhancing agents. The useful poly glycols have been those which are the reaction products of compounds such as ethylene oxide, propylene oxide, butylene oxide, ethylene glycol, diethylene glycol, etc.

It is noted, however, that while the aforementioned alkylene oxide polymers increase the speed of the silver halide photographic emulsion compositions containing said alkylene oxide polymers have an increased tendency to become fogged as compared with photographic emulsions which are not so sensitized. This fogging tendency is particularly pronounced when photographic film coated with an alkylene oxide polymer. The ethylene-diurea may above described alkylene oxide polymers is subjected to conditions such as prolonged development and storage at excessive temperatures and humidities.

Therefore, the incorporation of the speed enhancing agents necessitates the employment of rather large quantities of anti-foggants in order to overcome the great susceptibility to fogging of the sensitized photographic emulsion. While the use of the anti-foggant is advantageous to overcome the fogging difficulties, said anti-foggants offset the advantage of the use of the sensitizing agent in that said anti-foggants decrease the speed of the resulting silver halide emulsion. That is to say that when one uses an alkylene oxide polymer to increase the speed of the emulsion and then is forced to use an anti-foggant to eliminate the disadvantages of the speed sensitizer, said anti-foggant decreasing the speed of the silver halide emulsion with the resulting relatively small net increase in sensitivity of such a photographic emulsion.

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Therefore, it is an object of the instant invention to provide a sensitized silver halide photographic emulsion which has increased speed and/or contrast.

Another object of the instant invention is to provide a silver halide photographic emulsion which is sensitized with an alkylene oxide polymer and stabilized so as to eliminate the fogging effect of said polymer.

Yet, another object of the instant invention is to provide a stabilized silver halide photographic emulsion which is sensitized with an alkylene oxide polymer and stabilized with ethylene-diurea.

It has unexpectedly been found that when one employs in combination with an alkylene oxide sensitizing agent in a photographic emulsion ethylene-diurea having the structure

$$NH_2—CO—NH—CH_2—CH_2—NH—CO—NH_2$$

that the resulting emulsion does not possess the unfavorable effect of increased fogging. Furthermore, the combination of an alkylene oxide polymer and ethylene-diurea while it increases the sensitivity of the emulsion also improves the contrast and covering power of the developed silver.

Another advantage of the instant silver halide photographic emulsion system is the reduction of fog in high temperature processing as practiced in modern, automatic or semi-automatic processing machines. In these cases an appreciable speed increase is obtained even with the additional benefit of a fog reduction. The increased speed and reduced fogging tendencies are obtained by adding ethylene-diurea to a photographic emulsion which is sensitized with an alkylene oxide polymer. The ethylene diurea may be incorporated at any convenient time during the preparation of the silver halide emulsion. Thus, said ethylene-diurea may be incorporated prior to coating or subsequent thereto. That is to say the silver halide emulsion which is sensitized with an alkylene oxide polymer may have added thereto the ethylene-diurea during the formation thereof. It is preferred, however, to added the ethylene-diurea shortly before coating. The ethylene-diurea which is employed in connection with the instant invention may be prepared by the reaction of ethylene diamine and nitrourea in an aqueous solution as discussed by Davis et al., Journal of the American Chemical Society, 51, 1797 (1929).

The useful alkylene oxide polymers are all well known chemical substances. They may, for example, be the reaction product of an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide, etc., with a polyhydric alcohol such as ethylene glycol, diethylene glycol, nonaethylene glycol, decaethylene glycol, dodecaethylene glycol, ring dehydration products of hexitol, erythritol, 1,4-butyne diol, etc. In particular, the useful alkylene oxide polymers may be prepared by the methods disclosed in the Chemistry of Synthetic Resins, pages 990–994, published by Reinhold Publishing Corporation (1935).

The resulting product of the above reaction to form alkylene oxide polymers are poly glycols. The useful poly glycols should in general have a molecular weight in excess of 300 and preferably of about 1500 or to 4000 or more. If desired, the useful poly glycols may be further modified by reaction with various mono or poly-functional etherification or esterification agents to introduce lipophilic groups such as aliphatic hydrocarbon chains which may have from about 8 to about 18 carbon atoms or more. Typical aliphatic hydrocarbon chains of this type which may be incorporated into the poly glycols include such hydrocarbon chains as n-octyl, n-dodecyl, n-tetradecyl, n-octadecyl, n-eicosyl, etc. Furthermore, other useful lipophilic groups include fatty acid halides which contain from about 8 to 20 carbon atoms such as n-octadecoyl, n-dodecoyl, n-tetradecoyl, n-oleyl, etc.

Therefore, useful alkylene oxide polymers which may be employed in connection with the instant invention include, but are not limited to, are as follows:

Polyethylene oxide

$$HO\,CH_2\,CH_2\,O(CH_2\,CH_2O)_n\,CH_2\,CH_2\,OH$$

Di-(polyethylene-glycoxy)-decane

$$(CH_2)_{10}\begin{cases} O(CH_2CH_2O)_nCH_2CH_2OH \\ O(CH_2CH_2O)_nCH_2CH_2OH \end{cases}$$

Polyethylene oxide oleyl ether

$$HOCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OC_{18}H_{35}$$

Polyethylene oxide lauryl ether

$$HOCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OC_{12}H_{25}$$

wherein n is an integer greater than about 10.

As noted above, it has unexpectedly been found that when an alkylene oxide polymer and ethylene-diurea are combined in a silver halide photographic emulsion one obtains increased speed, covering power, and stability to fogging. The results obtained by this composition are not obtained by the use of either of the ingredients, i.e., an alkylene oxide polymer or ethylene-diurea, alone, and it is speculated that the combined effect of these two components is a synergistic one.

While the exact mode of operation of the instant invention is presently unknown, it is currently theorized that when ethylene-diurea and an alkylene oxide polymer are combined in a silver halide photographic emulsion they react in a synergistic manner to increase the speed, covering power and stability to fogging thereof. This is offered merely as a theory to explain the mode of operation of the instant invention and should not be construed in any way as imposing a limitation thereon.

In general, the ethylene-diurea may be employed in the instant composition in amounts from about 0.5 to about 5 grams per mol of silver halide in the emulsion. The preferred amount of ethylene-diurea which may be employed is about 2 grams per mol of silver halide emulsion. The silver halide emulsion of the instant invention may be prepared in any conventional manner, such as by emulsification and digestion or ripening of the silver halide, the elimination of aqueous salts by washing, and a second digestion or after-ripening to obtain increased sensitivity.

One standard procedure for preparing photographic silver halide emulsions is as follows.

(1) Precipitation, wherein the silver halide is precipitated by the interaction of a water-soluble silver salt and a water-soluble halide, in the presence of a carrier, e.g. gelatin.

(2) Digestion, wherein the above precipitate is heated for a period of time at a raised temperature, e.g. 50° to 60° C., with or without the addition of further carrier, e.g. gelatin.

(3) Washing, wherein the digested, solidified or set (e.g. by chilling) emulsion is washed to remove soluble salts.

(4) Melting out and second digestion, wherein the washed emulsion and the resulting flowable emulsion is heated for a period of time, with or without the addition of further carrier, e.g. gelatin.

Of course, variations of the above four steps can be employed. An emulsion, when used without employing a step, such as (3), we call an unwashed, emulsion. An emulsion when used following completion of all four steps, we call a washed, finished emulsion. The latter is the type of emulsion generally used.

During the last step of the above process, i.e. the second or final digestion, the emulsion increases in sensitivity. Various substances have been employed in the past to increase the speed of the photographic emulsion. These substances may be added during one of the digesting steps in the above process. Frequently, sulfur compounds such as the so-called sulfur sensitizers have been employed in connection with this type of emulsion. For example, compounds such as allyl isothiocyanate, thiourea, thiocarbanilide, etc., have been added. These and other useful additives are described in U.S. Patents 1,574,944; 1,623,499; and 2,410,689. In addition, the emulsion may be treated with salts of noble metals, such as ruthenium, rhodium, palladium, iridium and platinum. Furthermore, the emulsion may be chemically sensitized with gold salts as described in U.S. Patent 2,399,083 or stabilized with gold salts such as water-insoluble gold compounds which are added during one of the above-noted digestion steps in the preparation of the silver halide photographic emulsion. Generally, these gold stabilizing compounds have a solubility as low as 0.03 milligrams per 100 milliliters of water.

Useful compounds of this type are disclosed in U.S. Patents 2,597,856 and 2,597,915 and include compounds such as potassium chloroaurite, potassium aurothiocyanate, ammonium aurothiosulfate, potassium chloraurate and auric trichloride. In addition, the emulsion may be chemically sensitized with reducing agents. Polyamine compounds such as diethylene triamine, triethylene tetramine, tetraethylene pentamine or tetrapropylene pentamine may be employed for this purpose. In addition, the reducing agents such as stannous salts, imino- aminomethane sulfinic acid, hydrazine, hydroxylamine, formaldehyde sulfoxylate or sodium hydrosulfite may be employed as disclosed in U.S. Patents 2,487,850; 1,623,499 and Belgium Patent 547,323 and French Patent 1,146,955.

In connection with the instant invention, one may employ gelatin as the carrier in the silver halide emulsion in combination with other light-sensitive materials. In addition, one may use such carriers as polyvinyl alcohol, polyvinyl pyrrolidone, casein, carboxy methyl cellulose, hydroxyethyl cellulose, gums and other synthetic resins.

The present invention will now be described by reference to the following specific examples. Such examples are presented for purposes of illustration only, and the present invention is in no way to be deemed as limited thereto.

EXAMPLE I

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared by emulsifying and digesting the silver halide and subsequently eliminating the aqueous salts therefrom by washing. The emulsion was then digested again and brought up to its maximum light-sensitivity. Conventional additives including stabilizers, hardeners and surfactants were then added to the emulsion. A 10% solution of polyethylene oxide lauryl ether ("BRIJ 35," Atlas Powder Company, Wilmington, Del.) in water was prepared and added to the emulsion. In addition, a 10% aqueous solution of ethylene-diurea was also added to the emulsion. Samples of the emulsion containing about 0.6 mols of silver halide resulted. The emulsion samples were coated on a cellulose ester base and dried. The samples of these film coatings were then exposed in a type 1B Sensitometer and developed in a developer of the following composition:

Water—500 cc.
Metol—2.2 g.
Sodium sulfite, anhydrous—72.0 g.
Hydroquinone—8.8 g.
Sodium carbonate, monohydrated—56.0 g.
Potassium bromide—4.0 g.
Water to make 10. l.

As may be noted from the following table, the silver halide emulsion of the instant invention had increased covering power. The covering power is obtained by dividing the optical density at maximum density by the grams of silver per square decimeter in the developed image layer. This improved covering power was accomplished without lowering the melting point of the emulsion.

TABLE 1

Quantity of BRIJ 35 added (g.)	Quantity of ethylene-diurea added (g.)	Relative speed	Fog 12′	Covering power, $D_{max.}$[2] g. Ag/dm.
0	0	100	.24	36.5
1	0	150	.30	36.5
1	2	180	.17	41.0

EXAMPLE II

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide which was prepared as in Example I was coated on a film base. Subsequent to the coating, a solution containing 20 grams of gelatin in 1 liter of water, 1 gram of polyethylene oxide lauryl ether and 2 grams of ethylene-diurea was coated thereon as an anti-abrasion layer.

The results obtained when the film base was exposed to a Type 1B Sensitometer and developed in a developer having a composition as in Example I were identical with the results as obtained in Example I.

EXAMPLE III

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared and coated on a film base as in Example II, with the exception that the coating applied as an anti-abrasion layer did not contain ethylene-diurea. The results obtained after exposure and processing as described in Example I were similar to that obtained in Example I when no ethylene-diurea was added.

EXAMPLE IV

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared and coated on a film base as in Example II, with the exception that the abrasion layer did not contain either ethylene-diurea or polyethylene oxide lauryl ether. After drying and processing as in Example I, the results obtained were similar to Example I when neither the polyethylene oxide lauryl ether, nor the ethylene-diurea were present.

EXAMPLE V

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared as in Example I. The emulsion samples were coated on a suitable polyester base and dried. Samples of film coatings were then exposed and developed in a high temperature rapid processing M-6 X-Omat system with the following results:

TABLE 2

Quantity of BRIJ 35 added (g.)	Quantity of ethylene-diurea added (g.)	Relative speed	Fog 12′	Covering power, $D_{max.}$, g. Ag/dm.[2]
0	0	100	.30	36.5
1	0	100	.38	36.5
1	2	150	.30	41.0

As may be readily seen by the above data, the covering power of the composition of the instant invention was greatly improved over that of a composition which did not contain an alkylene oxide polymer and ethylene-diurea.

EXAMPLE VI

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared as in Example I. A 10% solution of polyethylene oxide oleyl ether was employed instead of the polyethylene oxide lauryl ether with the same results as obtained in Example I.

EXAMPLE VII

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared as in Example I. A 10% solution of polyethylene oxide was employed instead of the polyethylene oxide lauryl ether with the same results as obtained in Example I.

EXAMPLE VIII

A silver halide emulsion in gelatin containing 2 mol percent silver iodide and 98 mol percent silver bromide was prepared as in Example I. A 10% solution of di-(polyethylene glycoxy)decane was employed instead of polyethylene oxide lauryl ether with the same results as obtained in Example I.

Although we have referred throughout the present specification to the use of silver halide emulsions, and in particular silver iodide and silver bromide emulsions, it is to be understood that we intend to include, silver chloride, silver bromide and silver iodide either alone or in combination as the light-sensitive salt to which other sensitizing materials have been added. It is also to be understood that other modifications may be made in our process or materials without the parting from the invention, and they are intended to be taken limited only by the scope of the appended claims.

Suitable supports which can be employed in connection with the instant invention include such conventional support materials as cellulose ester supports including the hydrophobic variety or the type having a surface made hydrophilic by partial saponification metals such as aluminum or zinc, terephthalic acid ester polymers, paper, glass, film and the like.

I claim:

1. A stabilized photographic emulsion composition having a speed as great as or not appreciably reduced from that of the unstabilized but sensitized emulsion comprising:

(a) a colloidal carrier;

(b) a light-sensitive silver halide;

(c) an alkylene oxide polymer in an amount effective to sensitize the photographic emulsion; and

(d) ethylene-diurea of the formula:

$$NH_2—CO—NH—CH_2—CH_2—NH—CO—NH_2$$

in an amount effective to stabilize the photographic emulsion.

2. The composition as defined in claim **1** wherein the alkylene oxide polymer is polyethylene oxide lauryl ether.

3. The composition as defined in claim **1** wherein the colloidal carrier is gelatin.

4. The composition of claim **1** wherein said ethylene-diurea is present in an amount of from about 0.5 to about 5 grams per mol of silver halide.

5. A process for stabilizing a sensitized photographic emulsion without appreciably reducing the speed of the emulsion from that of the unstabilized sensitized emulsion which comprises adding to a photographic emulsion comprising a colloidal carrier, a light-sensitive silver halide and an alkylene oxide polymer in an amount effective to sensitize the photographic emulsion, ethylene diurea of the formula:

$$NH_2—CO—NH—CH_2—CH_2—NH—CO—NH_2$$

in an amount effective to stabilize the photographic emulsion.

6. The process of claim **5** wherein the alkylene oxide polymer is polyethylene oxide lauryl ether.

7. The process of claim **5** wherein said ethylene-diurea is present in an amount of from about 0.5 to about 5 grams per mol of silver halide.

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