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STABILIZATION OF PHOTOGRAPHIC EMULSIONS SENSITIZED WITH ALKYLENE OXIDE POLYMERS

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This invention relates to photographic emulsions and in particular to light-sensitive silver-halide emulsions sensitized with alkylene oxide polymers and containing therein polyvinyl pyrrolidone as a stabilizer and antifogging agent.

It is known that the sensitivity of photographic emulsions, i.e., light-sensitive gelatino silver-halide emulsions can be increased by incorporating in said emulsions various alkylene oxide polymers which act in a manner analogous to the so-called "sulfur" sensitizers such as allylthioureas, thiocyanates, sodium thiosulfate, sodium hyposulfite, and the like, and in this connection reference is made to U.S. Patents 2,400,532, 2,441,389 and 2,423,549.

It is likewise known that photographic emulsions containing the aforementioned alkylene oxide polymers as sensitizers have a greater tendency to become fogged when compared to photographic emulsions that are not so sensitized. This fogging tendency is particularly pronounced when photographic film, coated with a light-sensitive silver-halide emulsion containing the above described alkylene oxide polymers, is subjected to such conditions as prolonged development and storage at excessive temperatures and humidities. It, therefore, becomes necessary to employ rather large quantities of antifoggants in order to overcome the greater susceptibility to fogging of photographic emulsions sensitized with the alkylene oxide polymers. However, this remedy of using excessively high amounts of antifoggants partly offsets the speed advantage gained from the alkylene oxide polymers in the first place with the result that the net increase in sensitivity of such photographic emulsions is very slight.

It is accordingly an object of this invention to provide photographic emulsions with increased sensitivity.

Specifically, an object of this invention is to provide improved photographic silver-halide emulsions sensitized with alkylene oxide polymers and having low susceptibility to fogging on prolonged development and storage under conditions of high temperatures and humidities.

Other objects will appear hereinafter as the description proceeds.

The foregoing objects are attained by bringing poly-N-vinyl-2-pyrrolidone into operative association with the photographic emulsions stabilized with alkylene oxide polymers. The resulting emulsions possess the higher sensitivity of emulsions containing the alkylene oxide polymers but without their high fogging tendencies.

That poly-N-vinyl-2-pyrrolidone should inhibit or reduce fog is most unusual since it is known that this substance, while increasing the speed when used alone in photographic emulsion, has no effect on reducing the fog. It would appear, therefore, that the combination of poly-N-vinyl-2-pyrrolidone and alkylene oxide polymers co-act or operate in a synergistic manner when grouped in a photographic silver-halide emulsion, that is, the ethylene oxide polymers function as chemical sensitizers while the poly-N-vinyl-2-pyrrolidone prevents the fogging resulting as a side effect of the sensitizers.

It is to be understood, however, that the above explanation is merely offered as a theory to explain the mode of operation of this invention and is not to be construed as imposing a limitation or narrowing thereof.

Although the poly-N-vinyl-2-pyrrolidone can be incorporated at any convenient time during the preparation of the silver-halide emulsion, it is preferred to add it shortly before coating. The most useful concentrations of poly-N-vinyl-2-pyrrolidone ranges from 2 to 25 g. per mole of silver-halide in the emulsion; optimum concentration is about 6 g. of the stabilizer per mole of silver-halide.

The poly-N-vinyl-2-pyrrolidone as used herein is a product of the General Aniline and Film Corporation and is sold under the name of PVP, type NP (non-pharmaceutical) and is available in viscosities of K–20, K–30 and K–40, all of which are suitable for use as a stabilizer in the present invention. The letter K represents a function of the mean molecular weight of the compound and is derived from the Fikentscher formula

$$\frac{\log \eta_{rel}}{c} = \frac{75K_0^2}{1+1.5_0c} + K_0$$

wherein c is the concentration in g./100 ml. of solution, η_{rel} is the viscosity of the solution compared to the solvent and $K=1000K_0$.

The alkylene oxide polymers are known chemical substances and many are commercially available. They can be prepared in various ways. For instance, a common procedure is to react an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide, etc., with polyhydric alcohols such as ethylene glycol, diethylene glycol, nonaethylene glycol, decaethylene glycol, dodecaethylene glycol, ring dehydration products of hexitols, etc. For additional information on the preparation of the above substances, reference is made to "The Chemistry of Synthetic Resins," pages 990–994, published by Reinhold Publishing Corporation (1935).

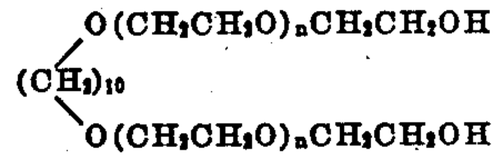
In general, the aforementioned poly-N-vinyl-2-pyrrolidone is useful for stabilizing all types of photographic silver-halide emulsions sensitized with alkylene oxide polymers. However, it has been found that superior results ensue when my stabilizer is incorporated in emulsions sensitized with alkylene oxide polymers of the class described in the previously cited patents. These alkylene oxide polymers are polyglycols and are prepared by reacting alkylene oxides with polyhydric alcohols, such as glycols, until the products have a molecular weight in excess of 300, preferably of 1500 or 4000 or more. The resulting polyglycols can be further modified by reacting with various mono-functional etherification or esterification agents to introduce lipophilic groups, e.g., an aliphatic hydrocarbon chain of 8 to 18 or more carbon atoms such as n-octyl, n-dodecyl, n-tetradecyl, n-octadecyl, and the like, and a fatty acid halide of 8 to 20 carbon atoms such as n-octadecoyl, n-dodecoyl, n-tetradecoyl, n-oleyl, and the like.

The following list illustrates typical alkylene oxide derivatives which can be used in combination with poly-N-vinyl-2-pyrrolidone to prepare fog free photographic silver-halide emulsions as described herein:

Polyethylene oxide

$$HOCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OH$$

Di-(polyethylene-glycoxy)-decane



Polyethylene oxide oleyl ether

$$HOCH_2CH_2O(CH_2CH_2O)_nCH_2CH_2OC_{17}H_{38}$$

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 and R is a fatty alkyl group having from 12 to 18 carbon atoms.

The silver-halide emulsions were prepared in the conventional way and comprise (1) emulsification and digestion or ripening of the silver-halide, (2) the elimination of aqueous salts usually by washing, (3) the second digestion or after-ripening to obtain increased sensitivity.

The combination of polyalkylene oxide polymers as stabilizers and poly-N-vinyl-2-pyrrolidone as an antifoggant for photographic silver-halide emulsions are effectual in the presence or absence of optical sensitizing dyes, color formers, or other addenda commonly incorporated in photographic emulsions.

My invention is not limited to silver-halide emulsions wherein the carrier is gelatin but may be incorporated with other light-sensitive materials wherein the carrier can be polyvinyl alcohol, casein, carboxy methyl cellulose, and the like.

The invention is illustrated in greater detail but not limited or restricted by the following example.

A silver-halide emulsion in gelatin containing 4% silver iodide and 96% silver bromide was prepared in a conventional manner and brought up to its maximum light-sensitivity. It was then readied for coating, finals were added such as sensitizing dyes, stabilizers and hardeners. A 10% solution of polyethylene oxide lauryl ether (a product sold by the Atlas Powder Company, Wilmington, Delaware, under the trade name "BRIJ 35") in water was prepared and added to the emulsion. Also, a 25% aqueous solution of PVP (NP: K–30) was prepared and added to the emulsion. The emulsion samples contained about 0.4 mole of silver-halide. The so prepared emulsion samples were coated on a suitable cellulose ester base and dried. Samples of these film coatings were then exposed in a Type IIB Sensitometer and developed in a developer of the following composition:

	G.
Metol	1.5
Sodium sulfite, anhydrous	45
Sodium bisulfite	1
Hydroquinone	3
Sodium carbonate, monohydrated	6
Potassium bromide	.8
Water to make 1 liter.	

Quantity of BRIJ Added, g.	Quantity of PVP Added, g.	Relative Speed	Fog 12'	Oven Fog 4'
0	0	100	.12	.18
1	0	160	.32	.26
1	2.5	160	.16	.18

I claim:

1. A photographic element comprising a support, at least one light-sensitive silver-halide emulsion layer comprising a silver-halide dispersed in a colloidal carrier selected from the class consisting of gelatin, polyvinyl alcohol, casein, and carboxy methyl cellulose, said emulsion layer containing in intimate contact with the silver halide grains thereof, a sensitizing quantity of an alkylene oxide polymer having a molecular weight of at least 300 and being selected from the group consisting of a polyalkylene glycol, a polyalkylene glycol ether wherein the ether group is an aliphatic chain of from 8 to 18 carbon atoms and a polyalkylene glycol ester wherein the ester group is an aliphatic chain of from 8 to 18 carbon atoms and as an antifogging agent for said emulsion layer and in intimate contact with the silver halide grains thereof 2 g. to 25 g. per mole of silver-halide in the emulsion of poly-N-vinyl-2-pyrrolidone having a K-value of from K–20 to K–40.

2. A photographic element as defined in claim 1 wherein the polyalkylene ether glycol is a polyethylene oxide lauryl ether.

3. A photographic element as defined in claim 1 wherein the colloidal carrier for the light-sensitive silver-halide is gelatin.

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