Patented Feb. 25, 1941 2,232,707

UNITED STATES PATENT OFFICE

2,232,707

STABILIZED PHOTOGRAPHIC SENSITIVE MATERIAL

John David Kendall, Ilford, England, assignor to Ilford Limited, Ilford, England, a British company

No Drawing. Application February 11, 1936, Serial No. 63,451. In Great Britain February 16, 1935

1 Claim. (Cl. 95—7)

This invention comprises improvements in or relating to the method of treating photographic materials comprising a light sensitive gelatin silver halide emulsion.

Photographic gelatin silver halide emulsions, as is well known, are relatively delicate and when stored under unfavourable conditions they may deteriorate rapidly. The deterioration may take several forms such as discolouration, growth of chemical fog or an undesirable change of gradation or sensitiveness.

Hitherto many additions have been made to emulsions for the purpose of stabilizing them or rendering them less sensitive to deterioration without impairing their photographic qualities; such additions, apart from soluble bromides and chlorides, include imidazoles and like compounds forming silver salts the solubility of which does not exceed that of silver chloride, quinine and quinidine and secondary and tertiary aromatic or aromatic aliphatic amines.

According to the present invention, a method of stabilizing photographic materials employing a light sensitive gelatine silver halide emulsion comprises treating the said material with a compound selected from the group comprising 2-mercapto-4-hydroxy pyrimidines, their alkyl, aryl and aralkyl substitution derivatives, their tautomeric compounds and their alkali metal and ammonium salts.

Examples of compounds which may be employed in accordance with the invention are 2-mercapto-4-hydroxy pyrimidines (thio-uracil), 6-methyl - 2 - mercapto- 4 - hydroxy pyrimidines (methyl-thio-uracil), 5.6.benz-2-mercapto-4-hydroxy-pyrimidines, their tautomeric compounds such as keto-tetra-hydro-thio-pyrimidines and their alkali metal or ammonium salts.

The compounds may be incorporated in the photographic emulsion, or they may be incorporated in the support for the sensitive emulsion layer or in an intermediate layer between the sensitive emulsion layer and the support such as the baryta coating commonly used in photographic papers, or they may be incorporated in a protective layer coated upon the emulsion surface, or the otherwise finished photographic material may be bathed in a solution containing the compound.

The materials which are normally used in close contact with light sensitive photographic material such as the wrapping materials used for photographic plates, films and the like may also be treated with these compounds either by incorporation in the material itself, bathing the material in a solution of the compounds or coating the material with a layer containing the compounds.

It is found that photographic materials treated in accordance with the invention show improvements in keeping qualities (that is reduction in fog produced by incubation and/or storage), the contrast remains more constant, and the rate of change of speed on storage is diminished.

In many cases the chemical fog produced on development of the unexposed emulsion is very much reduced, thus permitting the use of longer times of development, both at high and low temperatures.

The compounds may conveniently be added to an otherwise finished silver halide emulsion in the proportion of from about 1 to 100 ccs. of $\frac{1}{1000}$ solution per 500 grams of emulsion, representing approximately 10 gms. of silver nitrate in the case of slow emulsions as usually employed for preparing positive copies and from about 10 to 100 ccs. of a $\frac{1}{1000}$ solution per unit of emulsion equivalent to about 300 gms. silver nitrate in the case of fast emulsions such as are employed for the preparation of negatives.

The following examples illustrate by way of example methods of carrying the invention into effect.

Example I

A photographic paper coated with an ordinary gas light emulsion of soft contrast on development under standard conditions (namely in a metol-hydroquinone developer, as commonly used for gaslight emulsions) for one minute at 80° F. gave an initial fog of density 0.1, and the same material after incubation for ten days at 115° F. on development under the same conditions gave a fog of 0.18 density. Paper coated with the same emulsion containing an addition of 0.02 gm. of 6-methyl-2-mercapto-4-hydroxy-pyrimidine (methyl thio uracil) per 500 gms. of emulsion equivalent to about 10 gms. of silver nitrate developed under the same conditions gave a fog of 0.08 density and after incubation and development under the same conditions as above gave a fog of 0.08 density.

Example II

A photographic paper coated with a contrasty gaslight emulsion (silver chloride-gelatine) on development under the same conditions as in Example I, gave an initial fog density of 0.26, and the same material after incubation for ten days at 115° F. and developed under the same conditions gave a fog density of 0.6.

Paper coated with the same emulsion containing an addition of 0.02 gm. of 6-methyl-2-mercapto-4-hydroxy pyrimidine (methyl-thio-uracil) per 500 gms. of emulsion equivalent to about 10 gms. silver nitrate and treated under the same conditions as above gave a fog density of 0.1 initially and after incubation.

Example III

A photographic paper coated with an ordinary silver chlorobromide gelatin emulsion on forced development in a metol hydroquinone developer as commonly used for warm black papers, for two minutes at 100° F. gave a fog density of 1.0 and when developed for twenty minutes at 65° F. in the same developer gave a fog density of 0.10. The same material incubated for ten days at 115° F. and developed under the same conditions gave fog densities of 1.3 and 0.2 respectively. Paper coated with the same emulsion containing an addition of 0.016 gm. of 6-methyl-2-mercapto-4-hydroxy pyrimidine (methyl-thio-uracil) per 500 gms. of emulsion equivalent to about 10 grams of silver nitrate, and then developed under the same conditions as above gave fog densities of 0.2 and 0.04 respectively which were not increased by incubation.

Example IV

A photographic paper coated with a vigorous emulsion of the gaslight type was exposed under a step-wedge and developed under standard conditions in a metol-hydroquinone developer, as normally used for gaslight emulsions.

The gradation of the negative image was measured in the standard manner and the curve of density against log exposure was prepared. It was found that the mean slope of the curve was 4.11 and the maximum slope (gamma) 6.0. The same material exposed and developed under the same conditions after incubation for ten days at 115° F. gave a characteristic curve, the mean slope of which was 3.53 and the maximum slope 4.5. Paper coated with the same emulsion treated with an addition of 0.01 gm. of 6-methyl-2-mercapto-4-hydroxy pyrimidine (methyl-thio uracil) per 500 gms. of emulsion, equivalent to about 10 gms. of silver nitrate, exposed and developed under the same conditions gave a characteristic curve of 3.62 and 4.6 and this material after incubation gave a characteristic curve, the mean slope of which was 3.55 and the maximum slope 4.7. The speed changes on incubation of the untreated and treated material were not very great.

Example V

A photographic paper coated with a normal silver bromide emulsion such as are employed for preparing positive paper prints, on development under standard conditions for two minutes at 80° F. gave an initial fog density of 0.03 and required an exposure of 24 seconds compared to the standard 25 secs. The same material after incubation for ten days at 115° F. gave a fog density of 0.11 and required an exposure of 27 seconds.

Paper coated with the same emulsion containing an addition of 0.005 gms. of 2-mercapto-4-hydroxy pyrimidine (thio uracil) per 500 gms. of emulsion equivalent to 10 gms. silver nitrate on development under the same conditions gave an initial fog of density 0.02 and required an exposure of 29 seconds, and after incubation for ten days at 115° gave an initial fog of 0.03 density and required an exposure of 26 seconds.

Example VI

A photographic paper coated with an ordinary vigorous or contrasty gaslight emulsion, on development for one minute at 80° F. under standard conditions in a metol hydroquinone developer, as normally employed for gas light emulsions, gave an initial fog density of 0.11 and required an exposure of 5 seconds as compared with the standard 6 seconds. The same material on incubation for ten days at 115° F. gave on development under the same conditions an initial fog of 0.03 density and required an exposure of 5 seconds.

Paper coated with the same emulsion containing an addition of .01 gm. of 5.6-benz-2-mercapto-4-hydroxy pyrimidine per 500 gms. of emulsion equivalent to 10 gms. of silver nitrate treated under the same conditions gave an initial fog of 0.03 and on incubation for ten days at 115° F. gave an initial fog of 0.01 density, with no change in speed.

Example VII

Film coated with an ordinary gelatin silver iodobromide emulsion such as are employed for the preparation of negatives, on development under standard conditions, after being kept under normal storage conditions for two weeks, gave an initial fog of density .05, and samples of the same material kept for fourteen days in incubators at 125° F. and relative humidities of 15% and 54% and developed under similar conditions gave initial fog of densities .20 and .23 respectively. Samples of films coated with the same emulsion treated with an addition of 10 ccs. of $\frac{1}{1000}$ aqueous solution of 2-mercapto-4-hydroxy pyrimidine per unit of emulsion equivalent to 300 gms. silver nitrate and kept and developed under similar conditions gave on development initial fog densities of .05, .13, .12 respectively and the loss of speed was negligible.

Samples of films coated with the same emulsion treated with an addition of 20 ccs. of $\frac{1}{1000}$ aqueous solution of 2-mercapto-4-hydroxy pyrimidine per unit and kept and developed under similar conditions gave initial fog densities of .07, .09 and .08 respectively with a just perceptible loss of speed.

Example VIII

Samples of films coated with an ordinary gelatin silver iodobromide emulsion intended for the preparation of negatives after being kept for fourteen days under normal storage conditions and in incubators at 125° F. and relative humidities of 15% and 54% respectively gave on development under standard conditions initial fog densities of .10, .24 and .31 respectively. Samples of films coated with the same emulsion with an addition of 20 ccs. of $\frac{1}{1000}$ solution of 2-mercapto-4-hydroxy pyrimidine per unit of emulsion equivalent to 300 gms. silver nitrate, treated under the same conditions gave initial fog densities of .05, .06 and .09 respectively with very little loss of speed.

The addition of the stabilizing compounds to both silver chloride and silver chlorobromide emulsions has also been found to increase the stability of the contrast of the emulsions during incubation treatment and in some cases the contrast of the treated emulsion before incubation is higher than that of the untreated emulsion.

I claim:

A photographic emulsion comprising a gelatine silver halide emulsion having incorporated therein as a fog inhibiting agent, a small proportion of 6-methyl-2-mercapto-4-hydroxy pyrimidine.

JOHN DAVID KENDALL.