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PHOTOGRAPHIC EMULSIONS CONTAINING  
IMIDAZOLES

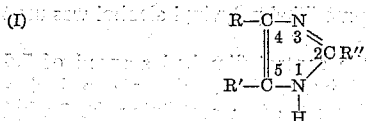
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**11 Claims. (Cl. 96-108)**

This invention relates to photographic emulsions having improved sensitivity and to a method for their preparation. More particularly it relates to photographic synthetic water-permeable colloid silver halide emulsions containing certain imidazoles in sensitizing amounts.

Photographic emulsions containing synthetic colloid binders are known. In one method for preparing such emulsions silver halide grains are formed in the absence of a protective colloid binder, the silver halide grains thus formed are ripened, activated by incorporation of a grain dispersing agent, and then a polymeric synthetic binder, such as polyvinyl alcohol, is added.

An object of this invention is to provide a new method for increasing the sensitivity of photographic silver halide emulsions in synthetic water-permeable colloid binders. A related object is to provide such emulsions which have improved photographic speed (light-sensitivity), gamma control, image tone, etc. A further object is to provide such a method and emulsions which are simple and utilize available and economical chemical compounds. Still further objects will be apparent from the following description of the invention.

It has been found that the sensitivity of light-sensitive silver halide emulsions utilizing synthetic water-soluble to water-permeable organic colloids having protective colloid properties can be enhanced by incorporating in the emulsion from 0.15 to 10%, based on the weight of the silver halide in the emulsion, of at least one imidazole corresponding to the formula:



wherein R, R' and R'' are the same or different and are taken from the group consisting of hydrogen, alkyl, preferably of not more than 12 carbon atoms, carboxyl or —COOM where M is alkali-metal, e.g., Na and K or ammonium. Suitable alkyl radicals, include methyl, ethyl, propyl, isopropyl, isobutyl n-butyl, decyl, tetradecyl and pentadecyl.

The photographic silver halide emulsions produced in accord with this invention are prepared by adding to a photographic emulsion having a synthetic binder, e.g., by the method of U.S. 2,752,246 from 0.15 to 10%, preferably 0.5 to 5%, by weight of the silver halide present in the emulsion, of an imidazole of the kind previously described. The photographic emulsions are conveniently prepared as follows:

A dispersion of silver halide grains is prepared in the absence of a protective colloid binder. Preferably, this is done by mixing a dilute aqueous solution of a soluble inorganic halide, e.g., ammonium bromide, potassium iodide, or potassium chloride, or mixtures of any of these, and a condensation product of an alkylene oxide and an alcohol or phenol as defined below, with a dilute aqueous solution of a water-soluble silver salt, e.g., silver nitrate, silver sulfate, silver sulfamate, silver citrate, silver acetate, or a mixture of two, three or more such salts. The alkylene oxide condensation product, mentioned above, is a nonionic surface-active dispersing agent containing at

least six intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom of oxygen, sulfur or nitrogen to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms containing an alkyl radical of at least 4 carbon atoms, and is used in an amount ranging from 1% to 30% of the weight of the silver halides. After the two solutions are mixed together, the mixture is allowed to ripen at ordinary or moderately elevated temperatures, e.g., 25° to 50° C., until the silver halide grains develop the desired size and shape. The ripened silver halide grains are then separated from soluble salts by decantation or by decantation followed by washing with water or by centrifugation until the silver halide grains have a specific conductivity in water, or in the finished emulsion, of the desired degree, e.g., less than 400 micromhos. The washed silver halide grains are then activated before any polymeric binder is added to the emulsion in order to develop maximum photographic qualities. This activation step consists in adding a dispersing agent or a non-optical photographic sensitizer, or both of these to the silver halide grains. The dispersing agent reduces fog in the final emulsion and assists in keeping the individual silver halide grains separated during the addition of binder and the coating operations, thus improving the photographic and physical quality of the finished film. The sensitizing agent imparts such desirable qualities to the final emulsion as improved photographic speed (light-sensitivity), gamma control, image tone, etc. It is preferred that the dispersing agent, if one is used, and the photographic sensitizer be added to the silver halide grains before bulking with polymeric binder to form the final emulsion. However, the exact order of adding the dispersing agent and the sensitizer is not important. Either the sensitizer or the dispersing agent can be added first or they can be added simultaneously, but preferably the sensitizer is added first. Examples of suitable dispersing agents used in this step include amine-modified polyvinyl alcohols derived from hydrolyzed vinyl ester/allyl glycidyl ether copolymers such as described in U.S. Patent 2,829,053 and polyvinyl acetals of aldehydes having a betaine group such as described in U.S. Patent 2,753,264. These dispersing agents are used in amounts ranging from 0.5% to 15% of the weight of the silver halides being treated. They are usually added in the form of an aqueous solution of 1-10% concentration. Suitable sensitizers for use in this activation step include sulfur sensitizers containing labile sulfur, e.g., sodium thiosulfate, allyl thiocarbamide, N-allyl thiourea and other compounds, e.g., gold thiocyanate, ammonium chloroplatinate, etc. These sensitizers are used in amounts of 0.005% or less based on the weight of the silver halides in the emulsion depending on the particular sensitizer being used. The activating step is preferably carried out at a temperature of about 40° to about 50° C. for periods ranging from 10 to 40 minutes. The imidazole sensitizer is conveniently added to the activated dispersion as a dilute aqueous solution in amount ranging from 0.15% to 10% by weight of the silver halide present, and the dispersion is mixed until it is uniform. However, the imidazole derivative may also be added simultaneously with the synthetic protective colloid binder described below or after the addition of the binder or before the activation step, but preferably the imidazole is added after activation. After the silver halide grains are redispersed and activated as described above, the dispersion is bulked with a synthetic polymeric protective colloid binder, e.g., polyvinyl alcohol, or a partially hydrolyzed polyvinyl carboxylic acid ester or a polyvinyl acetal having a sufficient number of intralinear  $-\text{CH}_2\text{CHOH}-$  groups to confer water-permeable characteristics, to provide a photographic emulsion having proper viscosity and other desired characteristics.

acteristics for coating on a support, e.g., transparent film base, glass plate, metal foil, or paper. The incorporation of the synthetic binder is usually carried out at temperatures ranging from 30 to 40° C. for a time sufficient to distribute the binder uniformly throughout the emulsion. The resulting emulsion can then be treated with coating aids, spreading agents, fog inhibitors, sensitizing dyes, etc., before it is coated on a conventional support.

The photographic emulsions of this invention and their methods of preparation are illustrated in further detail but are not limited to the following examples. The procedures described in these examples are carried out in the absence of actinic radiations and at room temperature, i.e., 20°–30° C., unless otherwise noted.

#### EXAMPLE I

##### Solution A:

46 cc. 3 N aqueous  $\text{NH}_4\text{Br}$   
5 cc.  $\frac{1}{2}$  N aqueous  $\text{KI}$   
25 cc. of a 10% solution of a condensation product of 1 mole of oleyl alcohol with approximately 20 moles of ethylene oxide  
50 cc. of water

##### Solution B:

32 cc. 3 N aqueous silver nitrate  
20% aqueous  $\text{NH}_3$  added to convert the silver to soluble compounds  
200 cc. water

Two sets of the above solutions were prepared and two similar precipitations were conducted under red safe lights by adding solution B to solution A over a period of about 30 seconds and with mild agitation at 30° C. The suspensions were stirred for  $\frac{1}{2}$  hour at 30° C. and were then allowed to stand at about 20° C. for an additional  $\frac{1}{2}$  hour to permit the silver halide grains to settle. The supernatant liquid was decanted and 50 cc. of water was added to each precipitate. The suspensions were stirred rapidly for 10 minutes at 30° C. to redisperse the grains and the two suspensions were combined and stirred an additional 5 minutes so that a single uniform suspension resulted. The suspension was heated to 45° C. and 10 cc. of 0.16% aqueous sodium thiosulfate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was added and ripened for 5 minutes. Three cc. of a gold thiocyanate solution containing 0.051% gold (prepared by adding 3 cc. of a 1% aqueous solution of  $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$  to 25 cc. of a 1% aqueous solution of ammonium thiocyanate) was then added and digested for an additional 20 minutes at 45° C., mild agitation being used throughout the digestion. The resulting digested silver halide emulsion was allowed to cool to 30° C. Two 25-cc. portions of this emulsion were then removed. To one of them there was added 5 g. of a 5% aqueous solution of imidazole, and the mixture was stirred 5 minutes at 30° C. The second portion served as a control, no imidazole being added.

Both portions were treated from this point in the same manner. Five grams of a 10% aqueous solution of an amine-modified polyvinyl alcohol (prepared by aminating vinyl acetate/allyl glycidyl ether copolymer with trimethylamine and hydrolyzing with sodium methylate, as described in U.S. Patent 2,829,053) was added to each portion and stirred at 30° C. for five minutes. This addition was followed by 85 g. of a 5% solution of a medium viscosity polyvinyl alcohol in aqueous ethanol solution containing 20% ethanol. The emulsion was then stirred at 30° C. for an additional 5 minutes. The pH of the emulsion was adjusted to 9.0 with dilute aqueous sodium hydroxide and the viscosity was adjusted to a convenient value by the addition of 20% aqueous ethanol. The solution was subsequently filtered through felt, and 2 cc. of a 1% aqueous solution of C-cetyl betaine was added as a spreading aid. The emulsion was coated on sub-coated cellulose acetate film base as described in U.S. 2,534,236 and the finished photographic film was dried.

Strips cut from the photographic films were exposed to blue light under a standard step-wedge and developed for 7 minutes at 20° C. under controlled standard conditions. After fixing, washing and drying by usual methods, the sensitometric properties of the films were determined. The speed of the control film was 6.9 units on an arbitrary scale while that of the film containing imidazole was 8.4 units on the same scale. On this scale an increase of one unit represents a doubling of the photographic speed so that the imidazole-containing emulsion was about three times faster than the control.

#### EXAMPLE II

The same procedure as in Example I was used, except as follows: (1) The suspensions were allowed to settle for 10 minutes instead of 30 minutes; (2) 45 cc. of water was added to each precipitate instead of 50 cc.; (3) 10 cc. of an aqueous gold thiocyanate solution containing 0.028% gold was used instead of 3 cc. of a 0.051% gold solution; (4) the additive for the digested emulsion was 5 g. of 5% aqueous imidazole 4,5-dicarboxylic acid just neutralized with sodium hydroxide and this solution was added after the amine-modified polyvinyl alcohol instead of before; (5) 5 g. of 5% aqueous amine-modified polyvinyl alcohol was used instead of 10 g. The processing steps for these films were the same as in Example I. The results showed a photographic speed of 6.3 for the control film as compared with 7.2 for the film containing the imidazole 4,5-dicarboxylic acid. This difference represents an increase of 0.9 unit or nearly two-fold over the control.

#### EXAMPLE III

The emulsion preparation was the same as that in Example I, except as follows: (1) 40 cc. 3 N  $\text{NH}_4\text{Br}$  was used in solution A instead of 46 cc.; (2) 45 cc. water was added to the precipitate instead of 50 cc.; (3) 4 cc. 0.5% aqueous sodium thiosulfate pentahydrate was used instead of 10 cc. of 0.16% aqueous sodium thiosulfate; (4) 2 cc. 0.056% gold solution was used instead of 3 cc.; (5) the ripening and digestion temperature for both sensitizers was 40° C. instead of 45° C.; (6) 5 g. of 5% aqueous 2-ethyl imidazole was used instead of imidazole; (7) 5 g. of 5% aqueous amine-modified polyvinyl alcohol was used instead of 10 g.

After processing, the control film had a speed of 7.5 units while the ethyl imidazole-containing film had a speed of 8.6 units so that the film containing the 2-ethyl imidazole was about 1.1 units higher or a little more than double the speed of the control film.

#### EXAMPLE IV

The emulsion preparation was the same as in Example I, except as follows: (1) the suspensions were allowed to settle for 10 minutes instead of 30 minutes; (2) 45 cc.  $\text{H}_2\text{O}$  was added to the precipitate instead of 50 cc.; (3) 5 cc. of an aqueous gold thiocyanate solution containing 0.028% gold was used instead of 3 cc. of a 0.051% Au solution; (4) four 25 cc. portions of the digested emulsion were removed, one served as a control, and to the other three was added (a) 5 g. of 5% aqueous imidazole, (b) 5 g. of 1% aqueous imidazole and (c) 5 g. of 0.2% aqueous imidazole respectively; (6) 5 g. of 5% aqueous amine-modified polyvinyl alcohol was used instead of 10 g.

After processing strips as in Example I, the relative sensitivities were:

|         | Sensitivity units |
|---------|-------------------|
| Control | 4.4               |
| A       | 5.6               |
| B       | 5.2               |
| C       | 5.2               |

where the numbers have the same meaning as in Example I. Thus, even at the low imidazole concentration a marked increase in sensitivity is obtained.

## EXAMPLE V

The emulsion preparation was the same as in Example I, except as follows: (1) The suspensions were settled for 20 minutes instead of 30 minutes; (2) 42 cc. H<sub>2</sub>O was added to each precipitate instead of 50 cc.; (3) 15 cc. of 0.16% aqueous sodium thiosulfate pentahydrate was used instead of 10 cc.; (4) 5 cc. of an aqueous gold thiocyanate solution containing 0.028% Au was used instead of 3 cc. of a solution containing 0.051% Au; (5) four 25-cc. portions of the digested emulsion were removed, one of which served as a control and 5 g. to 5% aqueous imidazole was added to each of the others at three different points in the preparation as follows: (a) before addition of amine-modified polyvinyl alcohol, (b) after addition of the amine-modified polyvinyl alcohol but before the addition of the polyvinyl alcohol, and (c) after the addition of the polyvinyl alcohol; (6) 5 g. of 5% aqueous amine-modified polyvinyl alcohol was used instead of 10 g.

After the processing of strips as in Example I, the following sensitivity data having the same meaning as in Example I were obtained:

|               | Sensitivity units |
|---------------|-------------------|
| Control ----- | 5.8               |
| A -----       | 6.8               |
| B -----       | 7.2               |
| C -----       | 7.3               |

It is apparent that an increase in sensitivity is obtained even though the imidazole is added after the addition of the polymeric binder.

The following comparative procedures show adverse effects of related imidazole derivatives which are not covered by the general Formula I.

## Comparative Procedure A

The emulsion preparation was the same as in Example I except that 5 g. of 5% benzimidazole in 10% aqueous alcohol, neutralized with HCl to increase solubility, was used in place of 5 g. of 5% aqueous imidazole in the digested emulsion. Strips developed as in Example I had the following sensitivities: control emulsion 8.9, benzimidazole-containing emulsion 7.1. This imidazole derivative decreased the sensitivity of the emulsion to nearly ¼ that of the control.

## Comparative Procedure B

Same procedure as in Example III, except that the amount of gold thiocyanate solution was 4 cc. of solution containing 0.056% Au instead of 2 cc., and the amount of imidazole derivative added to the digested emulsion was 0.1 g. of 4-methyl-5-nitroimidazole in 20 cc. H<sub>2</sub>O instead of 0.25 g. of 2-ethyl imidazole in 5 cc. H<sub>2</sub>O. After processing strips as in earlier examples, the measured sensitivities were: control film, 7.0; 4-methyl-5-nitroimidazole-containing film, 6.1. Thus the film containing the 4-methyl-5-nitroimidazole had only about ½ the sensitivity of the control film.

## Comparative Procedure C

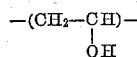
Same procedure as in Comparative Procedure B, except that the additive in this case was 0.02 g. of 1-methyl-4-nitro-5-cyanoimidazole in 10 g. H<sub>2</sub>O instead of the 4-methyl-5-nitroimidazole. The sensitivities of the strips were: control film, 7.3; experimental film, 6.0. Thus the film containing only a small amount of 1-methyl-4-nitro-5-cyanoimidazole had less than ½ the sensitivity of the control film.

As previously indicated, one, two or more imidazoles which correspond to general Formula I can be used in accordance with the invention. When more than one imidazole is used, the total amount is 0.15 to 10% of the weight of the silver halide. The preferred imidazoles are the unsubstituted and monosubstituted imidazoles because of their high degree of effectiveness as sensitizers.

Disubstituted and trisubstituted imidazoles constitute a useful class but they are less effective than the unsubstituted and monosubstituted imidazoles when employed in comparable concentration.

Examples of suitable imidazoles which can be used in accordance with this invention are 2-methylimidazole, 5-methylimidazole, 2,4-dimethylimidazole, 2-ethylimidazole, 2-butylimidazole, 2-ethyl-4-methylimidazole, 4-isobutylimidazole, 5-isopropylimidazole, 2-pentadecylimidazole, 2-tetradecylimidazole, 2-tridecylimidazole, 2,4,5-trimethylimidazole, 2-imidazolecarboxylic acid, 4-imidazolecarboxylic acid, 4,5-imidazolecarboxylic acid, and the like.

The photographic emulsions of this invention have been illustrated in the examples by specific reference to use of a polyvinyl alcohol as the synthetic polymeric binder. However, the imidazoles are also effective sensitizers for photographic emulsions containing other synthetic polymeric binders. For example, synthetic protective colloids such as low-substituted polyvinyl acetals, polyvinyl acetal colorformers, water-soluble polyamides, water-soluble cellulose derivatives, and the like can be used. Polyvinyl alcohol and polyvinyl acetals are a particularly preferred group of synthetic protective colloid binders for use in the emulsions of this invention. The vinyl alcohol polymers or synthetic hydroxylated polymers used in the preparation of the polyvinyl acetals include the well-known hydroxyl polymers prepared by polymerizing a vinyl ester such as vinyl acetate, vinyl propionate, vinyl benzoate, etc., alone or with minor proportions (10% or less) of an unsaturated copolymerizable monomer followed by partial or complete hydrolysis. Such polymers have a linear chain consisting predominantly of



groups. These polymers, as stated above, are water-soluble or hydrophilic in character and have at least 40 aliphatic hydroxyl groups per 100 chain atoms. The polymers, including copolymers, may have a minor number (e.g., 10% or less) of the hydroxyls modified with other groups, e.g., ether or ester groups. In the case of the copolymers, their partially hydrolyzed products, or the polymeric materials obtained by further reaction, e.g., esterification, etherification, or acetalization, it is necessary that at least 40 alcoholic hydroxyls be present for each 100 chain atoms, which are generally carbon. In the case of polyvinyl alcohol (completely hydrolyzed polyvinyl esters), there are a total of 50 hydroxyls to each 100 chain carbon atoms. For best results, the polymer should have a high molecular weight, e.g., at least 10,000 and preferably 35,000 or higher.

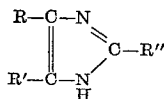
The photographic emulsions of this invention possess the important advantage over the hitherto known photographic emulsions having synthetic polymer binders of possessing enhanced or greater photographic speed. This is a very important practical advantage since it permits the manufacture of high-speed photographic emulsions having synthetic polymeric binders. Another advantage of the method of this invention is that it is simple and dependable and does not require tedious or complicated techniques or expensive chemicals.

What is claimed is:

1. A photographic emulsion comprising light-sensitive silver halide grains dispersed in an organic hydroxyl polymer having a molecular weight of at least 10,000 and protective colloid properties taken from the group consisting of polyvinyl alcohol and its partial carboxylic acid esters and acetals containing a sufficient number of intralinear  $\text{---CH}_2\text{CHOH---}$  groups to confer water-permeable characteristics, which emulsion has been ripened and digested and has added to the digested emulsion 0.15 to 10% by weight, based on the weight of the silver

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halide of at least one imidazole corresponding to the formula



wherein each of the radicals R, R' and R'' are taken from the group consisting of hydrogen, alkyl, carboxyl and —COOM where M is a member taken from the group consisting of alkali metal and ammonium.

2. An emulsion as set forth in claim 1 wherein said polymer is polyvinyl alcohol.

3. An emulsion as defined in claim 1 containing a sensitizer containing labile sulfur.

4. An emulsion as defined in claim 1 containing a non-ionic surface-active dispersing agent containing at least six intralinear oxyalkylene groups of 2 to 3 carbon atoms linked through an atom taken from the group consisting of oxygen, sulfur and nitrogen to a hydrophobic group including a hydrocarbon group of at least 8 carbon atoms embodying an alkyl radical of at least 4 carbon atoms.

5. An emulsion as defined in claim 1 wherein said imidazole is a 2-alkylimidazole wherein said alkyl radical contains 1 to 15 carbon atoms.

6. An emulsion as defined in claim 1 wherein the imidazole compound is imidazole.

7. An emulsion as defined in claim 1 wherein said imidazole is 4,5-imidazoledicarboxylic acid.

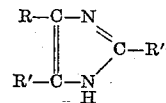
8. An emulsion as defined in claim 1 wherein said imidazole is 2-ethylimidazole.

9. A photographic element comprising a sheet support bearing at least one layer of a photographic emulsion as defined in claim 1.

10. A process which comprises admixing with a photographic silver halide emulsion containing an organic-

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hydroxyl polymer having a molecular weight of at least 10,000 and protective colloid properties taken from the group consisting of polyvinyl alcohol and its partial carboxylic acid esters and acetals containing a sufficient number of intralinear —CH<sub>2</sub>CHOH— groups to confer water-permeable characteristics as a binding agent for the silver halide grains, which emulsion has been ripened and digested, from 0.15 to 10% by weight based on the weight of the silver halide grains of at least one imidazole corresponding to the formula



wherein each of the radicals R, R' and R'' are taken from the group consisting of hydrogen, alkyl, carboxyl and —COOM where M is a member taken from the group consisting of alkali metal and ammonium.

11. A process as set forth in claim 10 wherein said polymer is polyvinyl alcohol.

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