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LOWER ALKYL LACTATE COUPLER SOLVENTS

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This invention relates to photography and, more particularly, to a method of incorporating photographic color couplers in light-sensitive silver halide gelatin photographic emulsions.

The use of color formers in photographic emulsions was first suggested in United States Patent 1,055,155 which issued to Rudolf Fischer in 1913. Fischer proposed a system of three layer color photography in which the couplers or color forming compounds were located in three different emulsion layers; wherein each coupler was capable of yielding, upon reaction with the oxidation products of a primary amino development agent, a dye image in a color complementary to the sensitivity of the layer in which it was incorporated. Although the Fischer process was theoretically feasible, it did not prove successful in practice. The couplers which were then available were not fast to diffusion and tended to migrate from the emulsion layer in which they were incorporated into an adjoining emulsion layer, thus causing a color degradation of the final dye images.

During the last three decades, numerous improvements were suggested which dealt with modified color formers and techniques for their incorporation in photographic colloids. By synthesizing couplers containing a bulky group, i.e., a long-chain alkyl radical (see United States Patent 2,186,849) attached to the molecule, their tendency to diffuse out of their respective sensitive emulsion layers was greatly reduced. The presence of this group imparts to the molecule a hydrophobic character. These long chain nondiffusing couplers also contain a salt-forming group, i.e., a carboxy or sulfo group which, in the form of their alkali salts, provides the couplers with water-soluble groups of hydrophilic character to permit their incorporation in aqueous gelatin silver halide emulsions. The simultaneous presence of hydrophilic and hydrophobic groups gives these color formers a soap-like character.

While the above process produces excellent dye images free from color degradation, the incorporation into the emulsion of long-chain high molecular weight couplers containing salt-forming groups poses a number of difficulties. In most instances, the color formers are dissolved in a water or water-alcohol solution of an alkali metal hydroxide such as aqueous sodium hydroxide or alcoholic potassium hydroxide, and then added to the emulsions as a so-called coating final as one of the last additives just prior to coating.

In most cases there is an extended but varying holding time between the addition of the color former solution to the silver halide emulsion and the actual application of the emulsions to the web or the film base. In many instances, there is a time interval between the completion of the remelting and the end of the coating operation which may range between two and six hours.

It is very important that during this holding time the viscosity be held constant because with the currently used coating techniques such as the dip-coat, metering-pan, or air-knife procedures any variation or drift in viscosity will result in different coating thicknesses. Thus, with a constant coating speed, an emulsion of lower viscosity will produce a thinner layer while a higher viscosity will result in a layer thicker than desired. Any change in thickness from standard will result in an unbalanced color picture; the thinner layer will give a lower maximum

density while a heavier layer will produce an undesirable higher maximum density in the layer being coated.

This increase in viscosity on holding and during coating is especially noticeable with emulsion formulations of relatively low water content and relatively high initial viscosity. These emulsions contain color formers resistant to diffusion which are substituted by a water-solubilizing group and employed in the form of a water-soluble alkali metal salt. Surprisingly, the degree of viscosity increase on holding depends to a large extent on the type of color former used. It is most pronounced with those color formers which contain a benzimidazole nucleus which is further substituted by a long-chain alkyl group attached to one of the nitrogen atoms and by a sulfonic or carboxylic acid group.

It is therefore an object of this invention to provide a method for the incorporation of color formers in photographic emulsions.

Another object of this invention is to provide a method of incorporating in a hydrophilic photographic colloid, color formers which are stable to diffusion and have an acid group as a substituent.

A further object of the invention involves the uniform distribution of a color former in a liquid photographic gelatin silver halide emulsion while insuring that the viscosity of said silver halide emulsion does not increase materially on holding.

A still further object of this invention comprises a light-sensitive gelatin silver halide emulsion containing a color former uniformly distributed through the gel matrix without the use of an alkali metal hydroxide solvent.

Other objects will be apparent from the following description.

These objects are accomplished by dissolving the color former fast to diffusion in a lower alkyl lactate in which the alkyl group contains no more than three carbon atoms, prior to adding them to the silver halide emulsion. Suitable alkyl lactates include methyl lactate, ethyl lactate, propyl lactate and isopropyl lactate, all of which are readily miscible with water and free from any obnoxious odor.

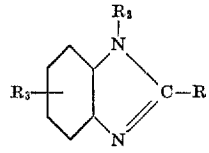
In preparing photographic emulsions, the color formers are first dissolved in the alkyl lactate; the resultant solution of the color former is then diluted with water or alcohol, e.g., methanol, ethanol, propanol, isopropanol or mixtures of water and alcohol. These diluents may also contain other coating finals. The aqueous alkyl lactate solution is then added directly and with adequate stirring to a melted gelatin silver halide emulsion. In a second method, the solution of the coupler in the alkyl lactate is first dissolved in an aqueous solution of a water-soluble colloid such as gelatin; and the resulting mixture is combined with a melted gelatin silver halide emulsion.

The amount of alkyl lactate employed varies somewhat with different color formers. In general, amounts ranging from 5 to 45 parts by weight of alkyl lactate per 10 parts by weight of color former have been found to be most satisfactory. The amounts of diluent may range from 2 to 8 parts of diluent per part of alkyl lactate.

In preparing the color emulsion for coating, the usual coating aids, stabilizers and wetting agents such as saponin and/or synthetic surfactants of the anionic, non-ionic or amphoteric type are added prior to the addition of the color formers. Among such wetting agents are those described in United States Patents 1,970,578, 2,118,059, 2,240,476 and 2,768,894.

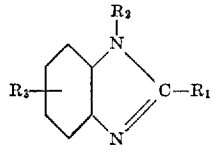
The color formers which have the strongest tendency to increase the viscosity on holding contain in their molecule a benzimidazole nucleus which is substituted on the nitrogen atom in the 1-position by an alkyl chain of at least 10 carbon atoms and substituted in the 5-position by a water

solubilizing group in which the benzimidazole nucleus is connected through it carbon atom in the 2-position to the residue of a color forming residue which is reactive with the oxidation products of a primary amino developing agent and contains a reactive methylene or ethenol or phenolic hydroxyl group. These color formers are characterized by the following general formula:

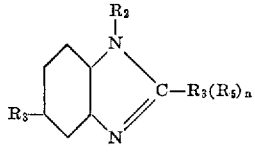


wherein R is a radical containing a reactive methylene, ethenol or phenolic hydroxyl group capable of reacting with the oxidation products or an aromatic amino developing agent to form an azomethine, indoaniline or phenazonium dyestuff; R_2 is an alkyl chain containing at least 10 carbon atoms, e.g., decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl and the like; and R_3 is a water solubilizing group such as sulfo, carboxy and the like.

More particularly, color formers which contain a benzimidazole nucleus as part of the molecule and which are capable of forming dye images upon development with a dialkylaminoaniline developing agent are illustrated by the following structural formulae:

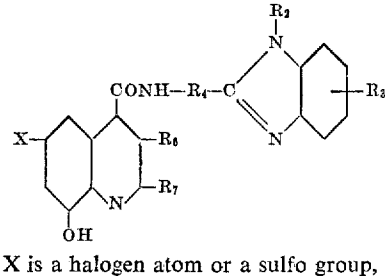


and



wherein R_1 is a hydroxy aromatic radical, such as substituted or unsubstituted hydroxynaphthyl, hydroxyphenyl and the like in which the hydroxy group is nuclearly attached, and said radical being linked to the benzimidazole radical in an ortho-position to said hydroxy group; R_4 is a phenyl radical; R_5 is the grouping —NH—$COCH_2A$, in which A is an alkyloyl radical, e.g., acetyl, propionyl, butyryl and the like, and an aroyl radical, e.g., benzoyl, naphthoyl and the like or a cyano or a carbethoxy group *n* is 1 or 2; and R_2 and R_3 have the same values as above. Suitable examples of color formers embraced by these general formulae are disclosed in United States Patents 2,545,687 and 2,547,307 in which their method of preparation is also described.

Color formers substituted by a benzimidazole nucleus and capable of forming magenta phenazonium (azine) dye images upon development with triaminobenzene developers are described in United States Patent 2,486,440; color formers used with N,N-dialkylphenylenediamine developers are disclosed in United States Patent 2,701,766. They are characterized by the following general formula:



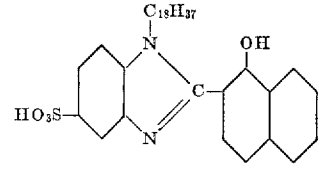
wherein X is a halogen atom or a sulfo group, R_2, R_3 and

R_4 have the same values as above; R_6 is hydrogen, a carboxyalkyl, allyl or lower alkyl group; and R_7 is an allyl, lower alkyl, aryl or heterocyclic group.

The invention is further illustrated by the following examples, but it is to be understood that the invention is not restricted thereto. The parts and percentages are by weight unless otherwise stated.

Example I

Two hundred grams of 1-octadecyl-2-[2'-(1'-hydroxynaphthyl)]benzimidazole-5-sulfonic acid which is characterized by the following structural formula:



was dissolved in 500 milliliters of methyl lactate. The resultant solution was diluted with 3,500 milliliters of water and added to ten kilograms of a liquid gelatin silver halide emulsion sensitized to red light and containing about 6 percent of gelatin, 3 percent of silver bromoiodide, plus small amounts of saponin and sodium tetradecyl sulfate as wetting agents.

In a control sample, 200 grams of color former was dissolved in 200 milliliters of 4 percent sodium hydroxide solution which was diluted with 3,800 milliliters of water prior to addition to the emulsion.

Viscosity measurements were taken at various holding times (37° C.) with the following results:

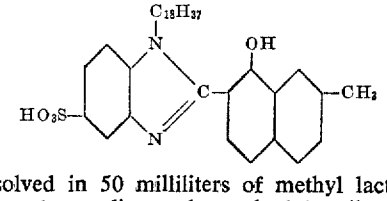
Control (Sodium Hydroxide)		Test (Methyl Lactate)	
Time	Relative Viscosity	Time	Relative Viscosity
0 Hour	82	0 Hour	65
1 Hour	101	1 Hour	65
2 Hours	139	2 Hours	66
4 Hours	183	4 Hours	66

It will be noted that the viscosity of the emulsion which contained the color former dissolved in methyl lactate remained substantially constant whereas the viscosity of the emulsion which contained the sodium hydroxide continued to increase with time.

The emulsion with the methyl lactate solvent was coated onto a base and dried. It gave a coating of even thickness and even maximum density after development. The control emulsion, due to its continued increase in viscosity, showed variations in the developed color densities between the start and the end of the coating.

Example II

Twenty grams of 1-octadecyl-2-[2'-(1'-hydroxy-7'-methyl)naphthyl]benzimidazole-5-sulfonic acid having the following structural formula:

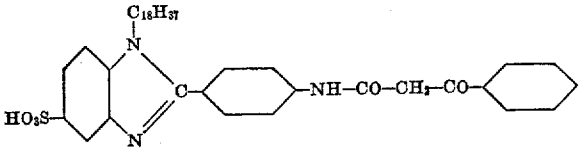


was dissolved in 50 milliliters of methyl lactate which was prepared according to the method described in United States Patent 2,581,050. The resultant solution was added with stirring to 300 milliliters of water containing 100 milligrams of the reaction product of 1 molar equivalent of 2,6,8-dimethylnonanol-4 and 12 molar equivalents of ethylene oxide, and 1 gram of saponin. The resultant dispersion was added to 1 kilogram of a silver bromoiodide emulsion having a gelatin concentration of 7 percent and a silver salt concentration of 3 percent. The

emulsion was held for six hours at 40° C. without an increase in viscosity. A control emulsion, in which the color former had been incorporated by the use of sodium hydroxide, showed a continued viscosity increase during the holding time and was completely gelled after 4 hours.

Example III

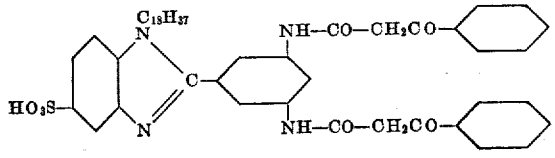
Example I was repeated except that a blue-sensitive silver halide emulsion was used which contained 20 grams of the yellow color former, 2-(4'-benzoylacetaminophenyl)-1-octadecyl-benzimidazole-5-sulfonic acid having the following structural formula:



which had been previously dissolved in 20 milliliters of isopropyl acetate and then diluted with 380 milliliters of water. The relative viscosity of this silver halide emulsion remained constant during 5 hours holding at 40° C. whereas a control emulsion prepared by dissolving the coupler in aqueous sodium hydroxide showed a relative viscosity increase of 90 percent.

Example IV

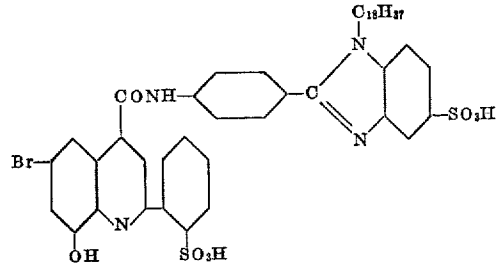
Twenty-five grams of 2-[(3',5'-dibenzoylacetamino) phenyl]-1-octadecylbenzimidazole-5-sulfonic acid having the following structural formula:



were dissolved in a mixture of 200 milliliters of ethyl-lactate and 300 milliliters of water and added to one kilogram of a blue-sensitive emulsion. Another 25 grams of the same color former were dissolved in 25 milliliters of 4 percent aqueous sodium hydroxide which was then diluted with 375 milliliters of water and added to one kilogram of the blue-sensitive emulsion. The viscosity of the emulsion containing the ethyl lactate did not increase during a four-hour holding period at 40° C. However, the viscosity of the material prepared with sodium hydroxide increased by about 110 percent during the same holding time.

Example V

Thirty grams of the magenta color former 2-[4-(6-bromo - 8 - hydroxy - 2 - (2'-sulfophenyl)-cinchoninoyl)-aminophenyl]-1-octadecyl-5-sulfonbenzimidazole having the following structural formula:



were dissolved in 300 milliliters of methyl lactate and diluted with 4 liters of water. The resulting solution was then added to 10 kilograms of a green sensitive silver halide emulsion which contained about 6 percent of gelatin and 2 percent of silver bromoiodide. The viscosity of the resultant emulsions remained substantially unchanged during a 4 hour holding time, whereas a type emulsion in which the color former had been dissolved by the use of

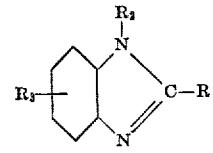
aqueous sodium hydroxide solution, showed a relative viscosity increase of over 75 percent.

While the present invention has been described with reference to certain preferred procedures, materials and uses, it is understood that the invention is not limited thereto and that numerous variations may be made in the procedure herein described and that equivalent materials may be substituted. For example, color formers and surface active agents other than those specifically mentioned and utilized in the foregoing examples may be used. Accordingly, we do not intend to be limited in the patent granted except as necessitated by the appended claims.

We claim:

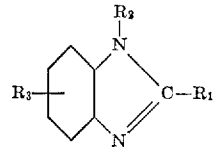
1. The method of incorporating in a light-sensitive gelatin silver halide emulsion, a color former fast to diffusion and capable of forming upon color development with a primary aromatic amino developing agent, a dye image selected from the class consisting of azomethine, indoaniline and phenazonium dye images, said color former containing a benzimidazole nucleus connected through its carbon atom in the 2-position to the residue of the color forming molecule which is reactive with the oxidation product of a primary developing agent and which contains a reactive group selected from the class consisting of a reactive methylene, ethenol and phenolic hydroxy group, said benzimidazole nucleus being substituted on one of the nitrogen atoms by an aliphatic hydrocarbon radical containing at least 10 carbon atoms and substituted in the benzene portion by a water solubilizing group which comprises dissolving 10 parts by weight of said color former in from 5 to 45 parts by weight of a lower alkyl lactate in which said alkyl group has from 1 to 3 carbon atoms, diluting the resultant solution with an aqueous solution containing a surface active agent, the amount of aqueous solution ranging from 2 to 8 parts by weight per part of alkyl lactate, and then adding the resultant dispersion to the liquid gelatin silver halide emulsion prior to coating it upon a suitable support.

2. The method of incorporating in a photographic gelatin silver halide emulsion layer, a color former stable to diffusion which is capable of forming with the oxidation products of a primary aromatic amino developing agent to yield upon exposure and development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dyes, said color former containing a benzimidazole radical and being selected from the group of compounds having the following general formula:

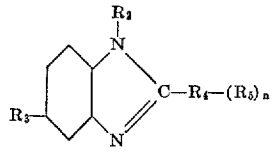


wherein R is the residue of the color forming molecule and contains a group selected from the class consisting of methylene, ethenol and phenolic hydroxy groups capable of reacting with the oxidation products of the primary aromatic amino developing agent; R_2 is an aliphatic hydrocarbon radical containing at least 10 carbon atoms; R_3 is a water-solubilizing group; and the carbon in the 2-position of said imidazole nucleus is linked to the residue of the color forming molecule which contains a reactive group selected from the group consisting of methylene, ethanol and phenolic hydroxy groups; which comprises dissolving 10 parts by weight of said color former in from 5 to 45 parts by weight of a lower alkyl lactate in which the alkyl has from 1 to 3 carbon atoms, diluting the color former solution thus obtained with an aqueous solution of a surface active agent, the amount of aqueous solution ranging from 2 to 8 parts by weight per part of alkyl lactate, and adding the resultant solution to a liquid gelatin silver halide emulsion prior to coating the latter upon a support.

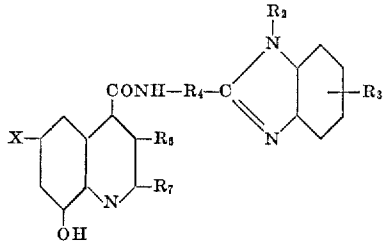
3. The method of incorporating into a gelatin silver halide emulsion layer a benzimidazole substituted color former selected from the class corresponding to the following formulae:



and



and



wherein R_1 is a hydroxy aromatic radical, the hydroxy group being nuclearly attached and said radical being linked to the benzimidazole nucleus in an ortho position to said hydroxy group; R_2 is an alkyl chain of at least 10 carbon atoms; R_3 is a water-solubilizing group; R_4 is a phenylene radical; R_5 is the group —NH—$COCH_2A$ in which A is selected from the group consisting of alkyloyl, aroyl, cyano and carbethoxy groups; R_6 is selected from the class consisting of hydrogen, carboxyalkyl, allyl and lower alkyl groups; and R_7 is selected

from the class consisting of lower alkyl, allyl, aryl, sulfophenyl and heterocyclic groups; *n* is selected from the class consisting of 1 and 2; and X is a member selected from the class consisting of halogen and sulfo groups; which comprises dissolving 10 parts by weight of said color former in from 5 to 45 parts by weight of an alkyl group on which said alkyl lactate has from 1 to 3 carbon atoms, diluting the color former solution thus obtained with a water solution of a surface active agent, the amount of aqueous solution ranging from 2 to 8 parts by weight per part of alkyl lactate, and adding the resultant dispersion to a liquid gelatin silver halide emulsion prior to coating the latter upon a suitable support.

4. The method of incorporating a color former into a gelatin silver halide emulsion layer as defined by claim 1, wherein said color former is 1-octadecyl-[2-2'(1'-hydroxynaphthyl)]benzimidazole - 5 - sulfonic acid, and wherein said alkyl lactate is methyl lactate.

5. The method of incorporating a color former into a gelatin silver halide emulsion layer as defined by claim 1, wherein said color former is 2-(4'-benzoylacetaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid, and wherein said alkyl lactate is ethyl lactate.

6. The method of incorporating a color former into a gelatin silver halide emulsion layer as defined by claim 1, wherein said color former is 2-[(3',5'-dibenzoylacetamino)phenyl]-1-octadecylbenzimidazole-5-sulfonic acid, and wherein said alkyl lactate is ethyl lactate.

7. The method of incorporating a color former into a gelatin silver halide emulsion layer as defined by claim 1, wherein said color former is 2-[4-(6-bromo-8-hydroxy-2 - (2' - sulfophenyl) - cinchonincyl) - aminophenyl]-1-octadecyl-5-sulfonbenzimidazole, and wherein said alkyl lactate is ethyl lactate.

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