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3,583,969

COLOR FORMERS FOR INCORPORATION IN PHOTOGRAPHIC EMULSIONS COMPRISING REACTION PRODUCT OF AN AQUEOUS ALKALINE GELATIN SOLUTION AND ALPHA-NAPHTHOLS, 1-ARYLPYRAZOLONES OR ACYLACETARYLIDES CONTAINING SULFO OR CARBOXY GROUPS

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5 Claims

ABSTRACT OF THE DISCLOSURE

Gelatin-hydrophilic color former adducts for use in silver halide color photographic emulsions, and silver halide emulsions and light-sensitive materials containing such adducts.

This invention relates to the preparation of gelatin adducts (i.e., addition products) of hydrophilic color formers employed in color photographic silver halide emulsions and light-sensitive materials containing such adducts.

Hydrophilic color formers are generally compounds of the alpha-naphthol, 1-arylpirazolone and acylacetylride series containing salt-forming sulfo acid or carboxy groups, which yield respectively cyan, magenta and yellow dyes by reaction with oxidation products of photographic color developers—especially N-substituted paraphenylenediamines, such as N-dialkylparaphenylenediamines. Such oxidation products and resulting dyes are formed in the areas in which silver halide is reduced to silver on development in a light-sensitive layer.

Heretofore, the aforesaid hydrophilic color formers were usually incorporated in silver halide photographic emulsions in the form of their alkali metal or ammonium salts, prior to coating of the emulsion on a film base or similar support. However, such salts have a strong tendency to crystallize from the emulsion, causing an undesirable increase in the viscosity of the emulsion and interfering with precision coating of thin layers. Moreover, the aforesaid color former salts cause an excessive rise in the pH of the emulsion, impairing its keeping qualities.

It is an object of this invention to provide derivatives of hydrophilic color formers which are soluble in aqueous silver halide photographic emulsions at a relatively low pH so as to avoid impairment of the keeping qualities of the emulsion, and which do not tend to crystallize from the emulsion, causing no substantial increase in its viscosity and permitting precision coating of thin layers.

We have found that gelation adducts of hydrophilic color formers containing salt-forming carboxy or sulfo groups can be prepared by mixing an alkaline solution of the color former and gelatin with an aqueous alcoholic solution of an acid in sufficient amount to render the mixture acidic. The gelatin adduct of the color former separates as a precipitate and can be recovered by filtration. After washing with water, it can be dissolved at slightly elevated temperatures in water to provide a solution having a pH of 6.5–7.5, suitable for addition to a silver halide photographic emulsion prior to coating. Aqueous solutions of the adducts are quite stable, yielding no precipitate on standing at room temperature for long periods, and their addition to photographic silver halide emulsions causes no material increase in the viscosity.

In preparing the adducts of this invention, the hydrophilic color former is preferably dissolved in water with

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sufficient alkali (e.g., an alkali metal hydroxide such as KOH or NaOH, or ammonium hydroxide), to yield an alkaline reaction (e.g., a pH of about 9–10). A minor proportion of alcohol (e.g. methanol or ethanol) may be included to facilitate dissolution of the color former salt. An aqueous gelatin solution is combined therewith, the amount of gelatin ranging from 0.25 to 5 parts and preferably from 0.5 to 2 parts by weight per part of the color former. The resulting solution is then mixed with an aqueous alcoholic solution containing a strong acid in excess of the amount required to neutralize the alkali. A mineral acid such as H₂SO₄ or HCl is preferably employed. The alcohol component of the solution is a monohydric alcohol which is water-miscible, e.g., methanol, ethanol, propanol or isopropanol—the amount being such as to yield an alcohol concentration in the combined mixture of 30 to 60% by volume. To ensure more complete precipitation, a gelatin coagulant such as polystyrene sulfonate can be included in small amount (e.g., up to about 0.25% by weight of the mixture).

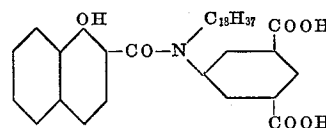
The amount of color former is suitably chosen from about 0.5 to 2% of the final mixture. The quantity of acid is preferably such as to yield—after neutralization of the free alkali as well as the alkali combined in the form of color former salt—a solution in which the excess acid is 0.05 to 0.5 N. The adduct which precipitates is filtered out at room temperature, and after washing with cold water, can be redissolved in water at slightly elevated temperature such as 40° C. while adjusting the pH to 6.5–7.5—usually by adding a small amount of an alkaline reactive compound. The color former concentration in such solutions ranges from 1 to 5% for purposes of addition to a silver halide photographic emulsion prior to coating on a film base.

The color formers employed can be any of the hydrophilic compounds of the alpha-naphthol, 1-arylpirazolone or acylacetylride series which contain carboxy or sulfo acid groups.

Our invention is illustrated by the following examples wherein parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

30 g. of cyan color former having the following formulation:



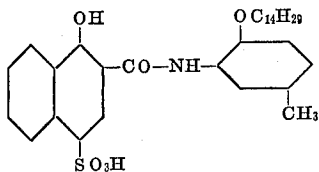
were dissolved in 100 ml. of 1.25 N aqueous NaOH solution, and the resulting mixture added to a solution of 15 g. gelatin in 500 ml. water at 40° C. The resulting mixture was then added to a solution of 1000 ml. water, 1000 ml. methanol, 40 ml. of 50% sulfuric acid and 5 g. of polystyrene sulfonate. The mixture was held at 15–25° C., and a flocculent precipitate of the gelatin adduct of the color former separated from the solution. It was recovered by filtration, washed with 4 portions, each 500 ml. of water at 20° C. The precipitate was then dissolved in 500 ml. of water at 40° C., adding sufficient NaOH to adjust the pH to 7.3.

EXAMPLE 2

The procedure of Example 1 was repeated, except that instead of the color former employed in that example, a

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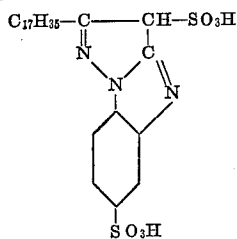
similar amount of a cyan color former was employed having the following formula:



A similar flocculent gelatin adduct of the color former separated from the solution and, after washing, was dissolved in 500 ml. of water at a pH of 7.3.

EXAMPLE 3

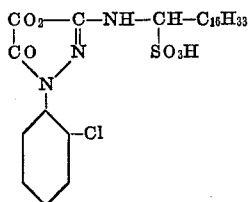
15 g. of a magenta color former having the formula:



were dissolved in 20 ml. methanol and sufficient NaOH added to provide a pH of 9. The resulting solution was added to a solution of 15 g. of gelatin in 500 ml. of water at 40° C. The resulting mixture was added to a solution of 1,000 ml. of water, 1000 ml. of methanol and 20 ml. of 50% sulfuric acid while maintaining the temperature at 15-25° C. A flocculent precipitate of a gelatin adduct of the color former separated and was recovered by filtration. After washing with 4 portions, each 400 ml., of water at 20° C., the precipitate was dissolved in 500 ml. of water at 40° C. with sufficient NaOH to adjust the pH to 7.3.

EXAMPLE 4

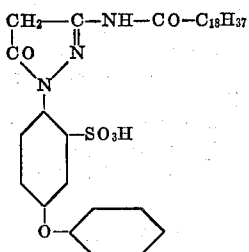
The procedure of Example 3 was repeated, except that instead of the color former there employed, there was substituted a similar quantity of a magenta color former having the following formula:



A similar flocculent gelatin adduct of the color former was obtained, and an aqueous solution thereof was similarly prepared having a pH of 7.3.

EXAMPLE 5

The procedure of Example 3 was repeated except that instead of the color former there employed, there was substituted a similar quantity of a magenta color former having the following formula:

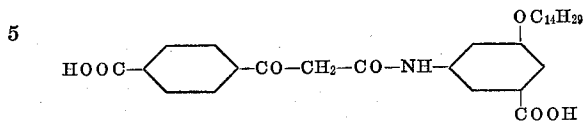


A flocculent precipitate of the color former adduct was obtained which yielded a solution in water at a pH of 7.3.

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EXAMPLE 6

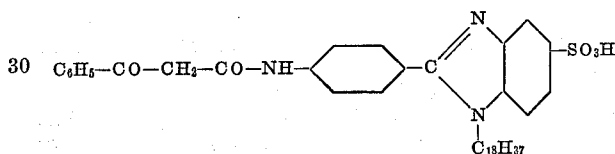
15 g. of yellow color former having the following formula:



were dissolved in 20 ml. of methanol, combined with 70 ml. of 1.25 N aqueous NaOH solution, and the resulting mixture added to a solution of 15 g. of gelatin in 400 ml. of water at 40° C. The resulting solution was added to a mixture of 1,000 ml. of water, 1,000 ml. of methanol, 20 ml. of 50% sulfuric acid and 5 g. of polystyrene sulfonate, and the temperature adjusted to 15-25° C. The resulting flocculent precipitate of gelatin-color former adduct was filtered off and washed with 3 portions, each 500 ml., of water at 20° C. The precipitate was then redissolved in 500 ml. of water at 40° C. with addition of sufficient NaOH to adjust the pH to 7.3.

EXAMPLE 7

The procedure of Example 6 was repeated, except that instead of the color former there employed, there was substituted a similar amount of a yellow color former having the following formula:



A flocculent gelatin adduct was obtained as in the preceding examples, and was dissolved, after washing, in water, adjusting the pH as before, to 7.3.

The solutions in water of adducts having a pH of 7.3, as prepared in Examples 1-7 inclusive were found to be stable on standing, showing no precipitation of color former or adduct after a period of two weeks.

EXAMPLE 8

500 ml. of the color former-gelatin adduct solution of Example 3 were added to 500 g. of a silver bromide-iodide gelatin photographic emulsion sensitized to green light. The emulsion was diluted with 1,000 ml. of water preparatory to coating. It was found to have a viscosity at 40° C. of 17 centipoises.

As a control, a similar emulsion was prepared using the same amount of the same color former, but in the form of its sodium salt instead of its gelatin adduct. The viscosity of the resulting emulsion at 40° C. was 29 centipoises.

Similarly advantageous results were obtained by adding the other color former-gelatin adduct solutions of the foregoing examples to similar amounts of the aforesaid silver bromide-iodide emulsion, sensitized in the case of the cyan color formers, to red light, and in the case of the yellow color formers, to blue light.

EXAMPLE 9

Silver halide-gelatin emulsions (e.g., silver chlorobromide- or silver bromoiodide-gelatin emulsions) sensitized respectively to red, green and blue light, were prepared as indicated in the foregoing example, including therein respectively, a gelatin adduct of a cyan, a magenta and a yellow hydrophilic color former respectively—the adducts being prepared as hereinabove illustrated. The emulsions were successively coated on a film base, such as subbed cellulose triacetate or polyethylene terephthalate, a yellow filter layer being interposed between the green-sensitive and the blue-sensitive layers. The resulting color film was exposed to a multi-colored image and developed in conventional manner, using first a non-color forming

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developer, such as p-methylaminophenol, and after a second overall light exposure, with a color developer such as N,N-diethyl-p-phenylenediamine. After bleaching out the silver with ferricyanide and fixing with sodium hyposulfite, a positive color transparency of the multi-color image is obtained.

Variations and modifications which will be obvious to those skilled in the art can be made in the foregoing examples, without departing from the scope of the invention.

We claim:

1. The method of preparing a gelatin adduct of a hydrophilic color former for color-photographic silver halid emulsions, which comprises mixing an aqueous alkaline solution of gelatin and a hydrophilic color former selected from the class consisting of photographic color formers of the alpha-naphthol, 1-arylpyrazolone and acylacetarylide series containing carboxy or sulfo acid groups, with an aqueous-monohydric water-miscible alcoholic solution of a strong acid which is present in excess of the amount required to neutralize the alkali contained in the gelatin-color former solution, the alcohol being sufficient in amount to yield a final concentration of 30-60% by volume in the mixture, and separating the resulting gelatin color former adduct which precipitates from the mixture.

2. A method as defined in claim 1, wherein the concentration of said color former in the said acidic aqueous alcoholic mixture is 0.5-2%, the quantity of gelatin is from 0.25 to 5 parts by weight per part of color former,

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and the excess acid contained in the final mixture is such as to yield a normality of 0.05 to 0.5.

3. A gelatin adduct of a hydrophilic color former for color photographic silver halide emulsions, prepared by the process of claim 1.

4. A method as defined in claim 1 wherein the hydrophilic color former is 2-(4'-benzoylacetyaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid.

5. A method according to claim 1 wherein the said acidic aqueous alcoholic mixture contains a small amount of polystyrene sulfonate.

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U.S. Cl. X.R.

96—100, 114

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,583,969 Dated June 8, 1971

Inventor(s) Guenther H. Klinger et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 5, change "Naphthols" to
-- Naphthols --

Signed and sealed this 29th day of February 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents