A method of incorporating a slightly water-soluble photographic ingredient containing a water-solubilizing group into an aqueous medium containing dissolved gelatin.

The method comprises the steps of:

1. Dissolving the photographic ingredient in a photographically inert organic liquid consisting essentially of tetrahydrothiophene-1,1-dioxide, N-methyl-2-pyrrolidinone, ethylene glycol, glycerol, acetonitrile or formamide.

2. Forming a dispersion of the photographic ingredient by mixing the solution obtained with an aqueous solution of a hydrophilic photographically inert colloid miscible with gelatin, more particularly a colloid of the following classes A to C i.e.

A. Water-soluble, natural colloid substances selected from the group of agar-agar, algamates, amylose and amylpectin.

B. Water-soluble modified natural colloid substances selected from the group of:

   - a. Non-ionic starches
   - b. Anionic starches
   - c. Water-soluble alginic acid derivatives
   - d. Non-ionic cellulose gums
   - e. Anionic cellulose gums

C. Synthetic water-soluble resins selected from the group consisting of vinyl polymers containing vinyl alcohol, N-binyllpyrrolidinone, vinyl methyl ether, acrylic acid and salts thereof, methacrylic acid groups and salts thereof, maleic acid salts thereof or acrylamide units, maleic anhydride, water-soluble polymers containing alkylene oxide units, water-soluble pre-polycondensates and polycondensate that are miscible with gelatin and selected from the group consisting of water-soluble urea-formaldehyde, water-soluble melamine formaldehyde, water-soluble guanamine-formaldehyde, water-soluble alkyd and water-soluble polyester resins, and

3. Homogeneously distributing the obtained dispersion into a gelatin solution or photographic gelatino silver halide emulsion.

2 Claims, No Drawings
METHOD OF INCORPORATING PHOTOGRAPHIC INGREDIENTS INTO A PHOTOGRAPHIC COLLOID

The present invention relates to the field of the preparation of photographic silver halide emulsion materials and more particularly to a method of incorporating photographic ingredients in a light-sensitive gelatin silver halide emulsion.

It has been known in the art (see e.g., the U.S. Pat. No. 3,050,394) to incorporate long chain nondiffusing color couplers containing a salt-forming group e.g., a carboxy or sulfonic group in an aqueous gelatin silver halide emulsion by dissolving said color couplers in a water, or a water-alcohol solution of an alkali metal hydroxide such as aqueous sodium hydroxide or alcoholic potassium hydroxide and adding the obtained solution as one of the last additives just prior to coating. Said technique asks for a special pH adjustment of the silver halide emulsion after addition of the alkaline solution.

The color couplers containing a water-solubilizing group such as a sulfonic acid (salt) group or carboxylic acid (salt) group cause an increase of the viscosity of colloid solutions containing gelatin. The increase in viscosity on holding is especially noticeable with gelatin solutions having a relatively low-water content and high-initial viscosity.

SUMMARY OF THE INVENTION

The present invention is directed to a process for incorporating photographic ingredients that are only slightly water-soluble and contain a water-solubilizing group, e.g., of the type of a sulfonic acid or carboxylic acid group in free acid or salt form in a gelatin silver halide emulsion. Said process comprises the steps of:

1. dissolving the photographic ingredient in a photographically inert organic liquid consisting essentially of tetrahydrodiphene-1,1-dioxide, N-methyl-2-pyrrolidone, ethylene glycol, glycerol, acetone or formamide,
2. forming a dispersion of the photographic ingredient by mixing the solution obtained with an aqueous solution of a hydrophilic photographically inert colloid miscible with gelatin more particularly a colloid of the following classes A to C.

a. water-soluble, natural colloidal substances selected from the group of agar-agar, alginates, amylose and amylepectine,
B. water-soluble modified natural colloid substances selected from the group of:
   a. nonionic starches
   b. anionic starches
   c. water-soluble algic acid derivatives
   d. nonionic cellulose gums
   e. anionic cellulose gums
   C. Synthetic water-soluble resins selected from the group consisting of vinyl polymers containing vinyl alcohol, N-vinylpyrrolidone, vinyl methyl ether, maleic anhydride, acrylic acid and salts thereof, methacrylic acid groups and salts thereof, maleic acid and salts thereof or acrylamide units, water-soluble polymers containing alkylene oxide units, water-soluble prepolycondensates and polycondensates that are miscible with gelatin and selected from the group consisting of water-soluble urea-formaldehyde, water-soluble melamine formaldehyde, water-soluble guanidine-formaldehyde, water-soluble alkyd and water-soluble polyester resins, and
3. homogeneously distributing the obtained dispersion into a gelatin solution or photographic gelatin silver halide emulsion.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention it is possible to prepare very fine particle dispersions of slightly water-soluble photographic ingredients containing a water-solubilizing group of the type of a sulfonic acid or carboxylic acid group in free acid or salt form in an aqueous medium comprising a hydrophilic colloid that is photographically inert and is compatible (miscible) with gelatin.

According to the process of the present invention it is more particularly possible to incorporate color couplers that are poorly water-soluble and contain a water-solubilizing group, salt forming or salt group from a concentrated stock solution without necessitating the use of alkali and a pH-adjustment of the silver halide emulsion. The use of a photographically inert protective colloid that does not interact like gelatin does with the photographic ingredient makes it possible to prepare stock solutions not suffering from viscosity changes during long storage time.

By slightly or poorly water-soluble photographic ingredient is meant a photographic ingredient such as a dye, e.g., a dye suited for use in a filter or antihalation layer, a color coupler, a mask-forming compound or a developing agent, that practically does not dissolve in water at room temperature although containing a water-solubilizing group, more particularly an ingredient that dissolves for at most 2 g per 100 ml of water at a temperature of 20°C.

The photographic ingredients suitable for incorporation into a photographic silver halide emulsion according to the method of the present invention may contain long chain residues to render them fast to diffusion in photographic colloid layers.

As water-soluble nonionic starches are particularly mentioned starch acetates, e.g., corn starch acetates containing 1 to 4 percent of acetyl groups.

starch hydroxethyl ethers.
hydroyl alkyl starch derivatives, e.g., hydroxethyl and hydroxypropyl starch derivatives.

Anionic starches are produced by the introduction of carboxyl, sulphonate salt, sulphonic acid or phosphoric acid groups into starch. This permits the preparation of water-soluble alkali metal or ammonium salts.

The class of nonionic cellulose gums includes, e.g., hydroxyalkyl cellulose derivatives and polyoxkylene cellulose derivatives.

Anionic cellulose gums are produced by the introduction of carboxyl, sulphonate salt, sulphonic acid or phosphoric acid groups into cellulose. This permits the preparation of the corresponding water-soluble alkali metal or ammonium salts.

As anionic cellulose gums are more particularly mentioned: carboxymethylcellulose, methyl cellulose-m-sulfobenzoate, ethyl cellulose-sulfoxuccinate and acetyl cellulose sulfoxuccinate.

As preferred synthetic water-soluble resins are mentioned copoly (styrene/maleic anhydride) (50/50), water-soluble homo- and copolymers of ethylene oxide and/or propylene oxide, e.g., the water-soluble alkylene oxide units containing polymers described in the U.S. Pat. specification No. 2,848,330 and the United Kingdom Pat. specifications Nos. 920,637—945,851—945,340 and 940,051 and further water-soluble melamine-formaldehyde resins.

It has to be noted that in the method of incorporating photographic ingredients into hydrophilic colloid according to the present invention the use of mixtures of the above-mentioned solvents in combination with mixtures of the above-cited water-soluble coloids is also included.

The amount of the water-soluble colloid(s) which are added to a gelatin silver halide emulsion together with the photographic ingredient can be comprised between 5 percent and 33 percent by weight in respect of the total weight of binder of the silver halide grains and is preferably between 15 percent and 25 percent.
The solvent or solvents can be removed by washing the gelled and noodled light-sensitive composition, or by evaporation from the gelled light-sensitive emulsion under vacuum.

Remaining amounts of the polar solvents used in the present invention do not cause desensitization or fogging of the light-sensitive silver halide emulsion.

DESCRIPTION OF PREFERRED EMBODIMENT

In preparing photographic color emulsions, the following preferred embodiment is applied.

A slightly water-soluble color coupler containing (a) sulphonic acid or (a) carboxylic acid group(s) in free acid or salt form is dissolved, normally by heating preferably between 50° and 80° C. in one of the said polar solvents or a mixture of such a polar solvent and a solvent having a dielectric constant at 20° C. lower than that of ethylene glycol, the less polar solvent however being present only in minor amounts (e.g., 5 to 10 percent by weight) and the solution obtained is thoroughly mixed with a solution of at least one of the said water-soluble high-molecular weight compounds which are dissolved in water or a mixture of water and one of the said polar solvents. Care is taken that the amount of water does not surpass the quantity at which a stable dispersion can no longer be obtained. Thus, a stable transparent composition can be formed, which can be stored for weeks. The said composition is preferably incorporated by stirring into the melted gel of the light-sensitive gelatin silver halide emulsion whereupon the composition obtained is gelled and the polar solvent(s) is (are) removed at least partially by washing the gelled composition with water.

The photographic coatings, when prepared according to the color coupler incorporating technique as described above, produce on color development very sharp, highly transparent colored images.

OTHER EMBODIMENTS AND MODIFICATIONS.

The use of a little wetting agent facilitates the dispersion of the photographic ingredient in the hydrophilic colloid medium. Examples of suitable wetting agents are saponin, arylalkyl sulphonates and polyoxyalkylene compounds, more particularly:

\[
H_2C\overset{\longrightarrow}{\text{(CH)\text{n}_{10-20}}}-S\overset{\longrightarrow}{\text{O}_{3}}Na
\]

wherein:

n is a positive integer from 5 to 50.

As solvents having a dielectric constant (e) lower than that of ethylene glycol (e=38.6 at 20° C.) and suitable for use in mixtures substantially consisting of the above strong polar solvents may be mentioned, e.g., ethanol, isopropanol, ethylene glycol monooxyethoxy ether, diethylene glycol monoethoxy ether, ethylene glycol monooxyethoxy ether, ethylene glycol monoacetoxy ether, ethylene glycol mono-n-butyl ether, diacetone alcohol, methyl ethyl ketone, tetrahydrofuran, dioxane and ethylene glycol dimethyl ether.

EXAMLES

The following examples illustrate the present invention without limiting it thereeto.

EXAMPLE 1

1 gm. of color coupler having the following structural formula:

\[
\text{HO-CONH-(CH)_{10-20}-CH_3}
\]

is dissolved at 60° C in 10 ml. of tetrahydrothiophene-1 : 1-dioxide. The solution obtained is added, while stirring, to a solution of 1 gm. of ethyl cellulose-\(\alpha\)-(\(\beta\)-sulpho) monosuccinate (DS ethoxy : 2.2, DS \(\beta\)-sulpho monosuccinic acid ester : 0.8, viscosity at 20° C. of a 2 percent solution in water : 4 cp.) and 1 ml. of saponine, in 10 ml. of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38° C. with 50 gm. of a red-sensitized silver bromoiodide emulsion containing 0.33 mole of silver bromide, 0.0075 mole of silver iodide and 80 gm. of gelatin per kg. of emulsion.

Then the emulsion is coated onto a cellulose triacetate support and the coating is dried at 40° C.

EXAMPLE 2

1 gm. of color coupler having the following structural formula:

\[
\text{HO-CONH-(CH)_{10-20}-CH_3}
\]

is dissolved at 50° C in 10 ml. of N-methyl-2-pyrrolidinone. The solution obtained is added, while stirring, to a solution of 1 gm. of hydroxy ethyl cellulose (DS : 0.85, MS : 1.33 and viscosity of a 2 percent aqueous solution at 20° C. : 11.2 cp.), and 1 ml. of saponine in 10 ml. of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38° C. with 50 gm. of a green-sensitized silver bromoiodide emulsion containing 0.33 mole of silver bromide, 0.0075 mole of silver iodide and 90 gm. of gelatin per kg. The emulsion obtained is allowed to cool and the obtained gel noodled and washed for 90 minutes with cold water. The noodles are then remelted at 50° C whereupon the emulsion is coated in the usual manner.

EXAMPLE 3

1 gm. of color coupler having the following structural formula:

\[
\text{HO-CONH-(CH)_{10-20}-CH_3}
\]

is dissolved at 50° C in 10 ces. of formamide. The solution obtained is added, while stirring, to a solution of 1 g. of methyl cellulose-m-sulphobenzoate (DS methoxy : 1.78, DS m-sulphbenzoic acid ester : 0.62, viscosity of a 2 percent aqueous solution at 20° C. : 3.5 cp.) and 1 ml. of saponine in 10 ml. of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38° C. with 60 gm. of a positive silver bromoiodide emulsion containing 80 gm. of gelatin, 0.33 mole of silver bromide and 0.0075 mole of silver iodide. The emulsion is coated onto a cellulose triacetate support and then dried at 40° C.

EXAMPLE 4

1 gm. of color coupler having the following structural formula:
is dissolved at 80°C in 10 ml of ethylene glycol. The solution obtained is added while stirring to a solution of 1 gm. of carboxy methyl amyllose (DS : 1.2, viscosity of a 2 percent aqueous solution at 20°C : 20 cp.) and 1 ml. of saponine in 10 ml of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38°C with 60 gm. of a positive silver bromoiodide emulsion containing 80 gm. of gelatin, 0.33 mole of silver bromide and 0.0075 mole of silver iodide. The emulsion is coated onto a cellulose triacetate support whereupon the coating is dried at 40°C.

EXAMPLE 5

1 gm. of color coupler having the following structural formula:

\[
\begin{align*}
\text{HO} & \quad \text{CONH}-(\text{CH}_2)_3-\text{CH}_3 \\
\text{SO}_3\text{Na} &
\end{align*}
\]

is dissolved at 80°C in 10 ml of glycerol. The solution obtained is added while stirring to a solution in 10 ml of water of 1 gm. of copoly (styrene/maleic anhydride)(50/50) (intrinsic viscosity [η] measured at 25°C in acetone : 0.22) and 1 ml. of saponine.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38°C with 60 gm. of a positive silver bromoiodide emulsion containing 80 gm. of gelatin, 0.33 mole of silver bromide and 0.0075 mole of silver iodide. The emulsion is coated onto a cellulose triacetate support whereupon the coating is dried at 40°C.

EXAMPLE 6

1 gm. of color coupler having the following structural formula:

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{HN} & \quad \text{COO} \\
\text{SO}_3\text{H} &
\end{align*}
\]

is dissolved at 60°C in 10 ml of dimethyl sulphoxide. The solution obtained is added while stirring to a solution of 1 gm. of hydroxy ethyl cellulose (DS : 0.85, MS : 1.33, viscosity at 20°C of a 2 percent aqueous solution : 11.2 cp.), and 1 ml. of saponine in 10 ml of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38°C with 60 gm. of silver bromo-iodide emulsion containing 0.33 mole of silver bromide, 0.0075 mole of silver iodide and 80 gm. of gelatin per kg. of emulsion.

The emulsion is coated onto a cellulose triacetate support whereupon the coating is dried at 40°C.

EXAMPLE 7

1 gm. of color coupler having the following structural formula:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{--(CH}_2)_3-\text{O} \\
\text{CH}_3 &
\end{align*}
\]

is dissolved at 60°C in 10 ml of formamide. The solution obtained is added while stirring to a solution of 1 gm. of NIKRULAN HW (Registered Trademark for a water-soluble melamine-formaldehyde textile resin of Cassella Farbewerke Mainkur A.G. Frankfurt (Main) W-Germany) in 10 ml of water.

A homogeneous and very fine dispersion of color coupler is obtained. The said dispersion is mixed at a temperature of 38°C with 60 gm. of a positive silver bromo-iodide emulsion containing 80 gm. of gelatin, 0.33 mole of silver bromide and 0.0075 mole of silver iodide. The emulsion is coated onto a cellulose triacetate support whereupon the coating is dried at 40°C.

EXAMPLE 8

1 gm. of color coupler as described in example 8 is dissolved at 60°C in formamide. The thus obtained solution is added while stirring to a solution of 1 gm. of methyl cellulose-m-sulphobenzoate (DS methoxyl : 1.78, DS m-sulphobenzoic acid ester : 0.62, viscosity of a 2 percent aqueous solution at 20°C : 3.5 cp.) in 5 ml of formamide. The solution obtained is mixed at a temperature of 38°C with a mixture of 60 gm. of a positive emulsion as described in example 8, 20 ml of water and 1 ml. of saponine. The thus prepared light-sensitive composition is coated onto a cellulose triacetate support and dried at 40°C.

EXAMPLE 9

1 gm. of color coupler as described in example 5 is dissolved in 5 ml of ethylene glycol. The obtained solution is added while stirring to a solution of 1 gm. of copoly(styrene/maleic anhydride) (50/50) (intrinsic viscosity [η] measured at 25°C.
in acetone : 0.22) in a mixture of 5 ml. of methanol and 5 ml. of water. The thus obtained solution is mixed at a temperature of 38° C. with a mixture of 60 gm. of a positive emulsion as described in example 8, 20 ml. of water and 1 ml. of saponine. The thus prepared emulsion yields very clear magenta images.

EXAMPLE 11
0.5 gm. of a dye having the following structural formula:

\[
\text{SO}_3\text{Na}
\]

\[
\text{NC} = \text{CH} - \text{CH}_3
\]

\[
\text{NC} - \text{CH}_3 - \text{CH}_2
\]

is dissolved at 50° C. in 15 ml. of N-methylpyrrolidinone. The solution obtained is added while stirring to a solution of 1 gm. of (poly-hydroxyethyl)-polyhydroxyethyl-methyl)-methyl cellulose in 30 ml. of N-methylpyrrolidinone. The solution obtained can be incorporated homogeneously into a melted gelatin gel (i.e., a gelatin sol or gelatin solution) or coated directly on a transparent support to the desired thickness in order to form an anthalation layer (absorption maximum 435 nm.).

EXAMPLE 12
Example 11 is repeated but in lieu of 1 gm. of the cellulose derivative, 1 gm. of the (β-dimethyl amino - ethyleneoxy propyl ester) - (γ-hydroxy - propyl ester) - (β-dimethyl aminoethoxy ester) - (β-dimethy laminoethoxy ether) of alginic acid is used.

EXAMPLE 13
0.5 gm. of the dye of example 11 is dissolved at 50° C. in 15 ml. of acetonitrile. The solution obtained is added, while stirring, to a solution of 1 gm. of methylcellulose in 30 ml. of water and 2 ml. of a 80 percent aqueous solution of n-dodecyl sodium sulphate. A very fine dispersion of the dye is obtained which can be homogeneously mixed with a melted gelatin gel or coated directly as a filter layer on a transparent support.

EXAMPLE 14
0.5 gm. of the dye of example 11 is dissolved at 50° C. in 15 ml. of formamide. The solution obtained is added, while stirring, to a solution of 1 gm. of hydroxyethyl cellulose (with DS=0.85, MS=1.33 and a viscosity of 2 percent aqueous solution at 20° C. of 11.2 cp.) in 30 ml. of formamide. The solution obtained can be incorporated homogeneously in a melted gelatin gel or coated directly on a transparent support to the desired thickness in order to form a yellow filter layer.

We claim:
1. A method of incorporating a slightly water-soluble photographic ingredient containing a water-solubilizing group into a gelatin solution or photographic gelatino silver halide emulsion comprising the steps of
   1. dissolving the photographic ingredient in a photographically inert organic water-miscible liquid consisting essentially of tetrahydrothiophene-1,1-dioxide, N-methyl-2- pyrrolidinone, ethylene glycol, glycerol, acetonitrile or formamide.
   2. forming a dispersion of the photographic ingredient by mixing the solution obtained with an aqueous solution of a hydrophilic photographically inert colloid miscible with gelatin, said colloid being selected from the group consisting of agar-agar, amylose, amylopectine, nonionic starches, anionic starches, water-soluble alginic acid derivatives, nonionic cellulose gums, anionic cellulose gums, synthetic water-soluble resins selected from the group consisting of vinyl polymers containing vinyl alcohol, N-vinylpyrrolidinone, vinyl methyl ether, maleic anhydride, acrylic acid and salts thereof, methacrylic acid and salts thereof, maleic acid and salts thereof or acrylicamide units, water-soluble polymers containing alkylene oxide units, water-soluble prepolycondensates and polycondensates that are miscible with gelatin and selected from the group consisting of water-soluble urea-formaldehyde, water-soluble melamine-formaldehyde, water-soluble guanamine-formaldehyde, water-soluble alkyl and water-soluble polyester resins, and
   3. homogeneously distributing the obtained dispersion into a gelatin solution or a photographic gelatino silver halide emulsion.
2. The method according to claim 1, wherein the photographic ingredient is a dye or a color coupler containing a water-solubilizing group being a carboxylic acid or sulphonic acid groups in free acid or salt form.

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