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M - (3 - METHYLSALICYLAMIDO) - BENZALDEHYDE POLYVINYL ACETALS AS PHOTOGRAPHIC COLOR COUPLERS

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6 Claims. (Cl. 95—6)

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This invention relates to color photography and more particularly relates to photographic elements bearing a color-yielding layer comprising m - (3-methylsalicylamido)-benzaldehyde polyvinyl acetals containing light-sensitive silver salts.

An object of this invention is to provide improved color-yielding photographic elements. A related object is to provide improved hydrophilic colloid color formed silver halide emulsion layers in photographic elements. A further object is to provide such layers which have improved spectral characteristics for cyan (blue-green) dye images. Still other objects will be apparent from the following description of the invention.

It has been found that photographic colloid silver halide emulsion layers for the production of blue-green indoaniline dye images can be made by incorporating light-sensitive silver halides with an aqueous solution of an acetal of a water-soluble or hydrophilic hydroxyl polymer containing a plurality of recurring intralinear vinyl alcohol

$$(-CH_2-\underset{|}{C}HOH)$$

polymer unit groups with m-(3-methylsalicylamido) benzaldehyde in which 0.75 to 7.5% of the hydroxyl groups of such polymer are acetalized by this aldehyde. The aqueous solutions which are light-sensitive silver halide colloid emulsions after preparation can then be ripened, chilled, precipitated or gelled, digested and modified by the addition of more of such polymer and general emulsion sensitizers, anti-fogging agents, spectral sensitizing dyes, preservatives and/or other adjuvants and coated onto a temporary or permanent support or onto a layer of a photographic support, e. g., a hydrophilic hydroxyl polymer color former silver halide emulsion which yields a different subtractive color, e. g., magenta or yellow.

The silver halide emulsions in said polymer can be made by admixing an aqueous solution of a color-forming acetal of the above description with an aqueous solution of a water-soluble metal halide, e. g., ammonium bromide, and then with an aqueous solution of a soluble silver salt, e. g., silver nitrate. The resulting silver halide emulsions or dispersions, after suitable treatment such as coagulation, ripening, washing, and digesting, are coated from an aqueous solution, which may contain methyl or ethyl alcohol, onto a suitable support such as a film base or support which may be paper, glass, metal, or a cellulose ether or ester or a synthetic resin, e. g., polyvinyl acetal; nylon, etc. Sensitizing dyes can be incorporated into the compositions before coating, or the resulting layers can be bathed or impregnated with a solution of a sensitizing dye in acetone or alcohol.

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The polymeric color-forming acetal as defined above can also be mixed with other water-soluble polymers, e. g., gelatin, polyvinyl alcohol, and the water-soluble polyamides of McQueen and Weaver, Ser. No. 623,458, now Patent 2,465,109, prior to or during the preparation of photographic emulsions and the fabrication of photographic elements therefrom. Such color-forming acetal/water-soluble polymer mixtures can also be used as silver-free layers laid down in juxtaposition to emulsion layers, according to the disclosure of U. S. Patent 2,397,452.

The color-forming acetals are amorphous high-molecular weight solid polymers which are insoluble in dilute caustic, hot dimethylaniline, and hot water, and are soluble in 10 to 40% aqueous ethanol. The water-sensitivity and solubility of the color-forming polyvinyl acetals can be enhanced by the introduction of solubilizing groups. For example, carboxylic or sulfonic acid groups can be introduced by acetal formation with phthalaldehydic acid, o-sulfobenzaldehyde, or glyoxylic acid. These groups can be introduced into the polymer either before or after the introduction of the color-forming groups, as taught in application Ser. No. 19,155, filed April 5, 1948, now Patent 2,489,655.

The novel color-forming acetals used in the color-yielding silver halide emulsion layers and elements in accordance with this invention are described and claimed in application Ser. No. 19,155. For the sake of convenience their preparation is described here as follows: A suspension of the hydroxyl polymer in ethylene glycol, e. g., polyvinyl alcohol and m-(3-methylsalicylamido) benzaldehyde ethylene glycol acetal having dissolved therein a small proportion of an acidic catalyst, e. g., phosphoric acid, is heated with agitation at 60° C. to 80° C. for a period of 0.5 to 25 hours and the resulting acetal of polyvinyl alcohol with m-(3-methylsalicylamido)-benzaldehyde is then isolated. The isolation is accomplished by the addition of an ethylene glycol miscible solvent which is not a solvent for the polymeric acetal, e. g., acetone or methanol, followed by filtration and, if desired, by washing with such a latter solvent.

In order to obtain a polyvinyl acetal whose color and solubility do not change on standing, it is desirable to treat the slurry of the polyvinyl acetal color former with a compound capable of

neutralizing the acid catalyst. Suitable compounds for this process include alkoxides, alkali metal hydroxides, bicarbonates and carbonates; ammonia and its mono-, di-, and trialkyl substituted compounds, such as methylamine, dimethylamine, ethylamine, triethylamine, triethanolamine, etc.; heterocyclic bases, such as quinoline, pyridine, etc. The quantity of neutralizing agent added to the suspension should be sufficient to bring the pH to a value of about 6 to 8, preferably 7.5. The acid neutralizing compound may be dissolved in the solvent used during the dilution of the ethylene glycol reaction mixture, or may be added during any of the subsequent slurrying steps.

The m - (3 - methylsalicylamido) benzaldehyde ethylene glycol acetal is a colorless, crystalline compound which has a melting point of 134° to 135° C. It forms the subject matter of application Ser. No. 13,523, filed March 6, 1948, which matured into U. S. Patent 2,518,704 on August 15, 1950, and can be made after the manner disclosed in said application and as follows:

To a mechanically stirred suspension of 46 parts of 3-methylsalicylic acid in 120 parts of thionyl chloride there was added dropwise 1.5 parts of pyridine. After stirring at 25° C. for 1.5 hours, a homogeneous solution was obtained. The excess thionyl chloride was removed under reduced pressure and the acid chloride was dissolved in 60 parts of anhydrous dioxane and was added dropwise to a mechanically stirred mixture of 52 parts of potassium carbonate, 50 parts of m-aminobenzaldehyde ethylene glycol acetal, 200 parts of water and 60 parts of acetone maintained at 0° C. by means of external cooling. After dilution with water, the colorless crystals were collected, washed with cold water, and air dried. Crystallization of the compound from methylene chloride gave 68 parts of colorless crystals melting at 134–135° C.

The invention is further illustrated by the following examples wherein all parts are by weight, and solutions aqueous, unless otherwise indicated. All radiations which will expose or fog the light-sensitive silver halides are excluded.

Example I

To 10 parts of the polyvinyl acetal obtained from polyvinyl alcohol, having 5.8% of the hydroxyl groups acetalized with m-(3-methylsalicylamido) benzaldehyde ethylene glycol acetal and having an additional 3.9% of the hydroxyls acetalized with o-sulfobenzaldehyde prepared as described in Example I of application Ser. No. 19,155 was added 30 parts of ethanol, 150 parts of water, and a sufficient volume (about 1 part of 10% potassium hydroxide solution) to adjust the pH of the suspension to about 7.5. After stirring at 80–85° C. for one-half hour, a homogeneous solution was obtained which was filtered by suction through a coarse filter paper. The resulting solution was diluted to 200 parts with water and was used to prepare a silver halide emulsion under conditions which would not expose or cause fogging of the sensitive silver salts as follows:

To 100 parts of the above solution was added 40 parts of ethanol. This solution was stirred at 40° C. while solutions of (1) 31 parts of 3 N ammonium bromide, 2 parts of 0.5 N potassium iodide, and 32 parts of water, and (2) 29 parts of 3 N silver nitrate, 25 parts of 20% ammonium hydroxide, and 7 parts of water were added simultaneously and at equivalent rates during 7 minutes. After stirring for a total of one-half hour, the emulsion was run into 250 parts of 15% sodium sulfate solution. The precipitated emulsion was collected, divided into small pieces and washed for 1 hour in running water after which the excess water was drained off. The color-forming emulsion was dissolved by stirring at 75° C. for 15 minutes with 30 parts of ethanol and 35 parts of water, after which time the remaining 100 parts of the original polyvinyl acetal solution was added and the stirring continued for 15 minutes. After cooling to 35° C. the emulsion was coated on baryta-sized white paper. The resulting paper was exposed to form a latent image and then developed in a solution of the following composition:

Ingredients:	Parts
p-Aminodiethylaniline hydrochloride	2
Sodium sulfite (anhydrous)	10
Sodium carbonate (monohydrate)	20
Potassium bromide	2
Water to make	1000

The paper was then fixed in 25% aqueous sodium thiosulfate, washed, bleached in 4% potassium ferricyanide, washed, fixed in 25% sodium thiosulfate and washed. The resulting paper contained a bright, strong blue-green dye image.

Example II

The polyvinyl acetal described in Example III of application Ser. No. 19,155, having 1.47% and 0.195% of the hydroxyl groups acetalized with m-(3-methylsalicylamido) benzaldehyde ethylene glycol acetal and o-sulfobenzaldehyde sodium salt, respectively, was used to prepare a silver halide emulsion essentially as described in Example I. The redissolved emulsion was coated on film base and after processing a piece of exposed film essentially as described in Example I, a blue-green image was obtained.

Example III

Ten (10) parts of the polyvinyl acetal having 5.8% of the hydroxyl groups acetalized with m-(3 - methylsalicylamido) benzaldehyde ethylene glycol acetal and having an additional 2.3% of the hydroxy groups acetalized with o-sulfobenzaldehyde sodium salt (prepared as described in Example I of application Ser. No. 19,155) was used to prepare a 5% solution of the polyvinyl acetal essentially as described in Example I. The resulting solution was used to prepare a silver halide emulsion by the procedure described in Example I. The emulsion was coated on film base at a coating weight corresponding to 69.2 mg. of silver per sq. decimeter. A piece of exposed film processed as described in Example I gave a strong blue-green dye image having a maximum color density in excess of 5.0 when measured at 690 mμ, the point of maximum absorption for the dye.

In place of the specific aromatic amino color-developing agents disclosed in the examples, there may be substituted other specific agents of this type. Such agents include the mono-, di-, and tri-aminoaryl compounds and compounds formed therefrom by substitution in the amino groups as well as in the ring. The preferred developing agents in the process of dye coupling development are derivatives of p-phenylenediamine, and particularly the asymmetric di-N-substituted p-phenylenediamines, for example, p-aminodimethylaniline, 2 - amino - 5 - diethylaminotoluene, etc. These aromatic amino developing agents may be used in the form of their

salts which may be organic or inorganic. These salts are in general more stable than the free bases. As examples of suitable salts which might be mentioned are the hydrochloride, sulfate, oxalate, etc.

The photographic layers may also contain the usual sensitizers such as the cyanines and carbocyanine salts and bases and the cyazines and carbocyazine salts and bases employed to extend the sensitivity of the photographic emulsions.

The coupling compositions of the invention may also be used in the preparation of positive dye images by developing an exposed silver halide emulsion with a non-coupling developer, then exposing to light and developing with a coupling aromatic amino developer, i. e., by a color reversal process. Removal of the metallic silver by conventional methods yields a positive dye image.

The m-(3-methylsalicylamido) benzaldehyde polyvinyl acetal silver halide compositions can be used either in conjunction with other water-permeable colloids, e. g., photographic gelatin, but is preferably used as the sole binding agent for the silver salts.

Color-forming polyvinyl acetals of the described type which have less than 0.75% of the hydroxyls of the polyvinyl alcohol acetalized have an insufficient number of color-forming groups present to give sufficient color strength in the photographic color film. This degree of acetalization permits a theoretical top color density of only 1.8 in a film having a thickness of 5 microns (a practical coating thickness for multi-layer films), even if conversion of color former to dye is quantitative. This color density represents the lower limit of practical usefulness. If more than 7.5% hydroxyls of the polyvinyl alcohol are acetalized, the permeability of the resulting photographic layer to the various solutions used to process the color-forming photographic composition becomes too low for practical application. For example, if 10% of the hydroxyls are so acetalized, which is insufficient to effect alkali-solubility of the composition, the permeability of the resulting photographic element to processing solutions is so drastically reduced that satisfactory color development and particularly fixing cannot be obtained even by doubling processing times. The polyvinyl acetals falling within the range of this invention are outstanding with respect to top color density, spectral characteristics in the blue-green range on color development with p-phenylenediamine-type developers, light stability, processing characteristics, and availability of starting materials. In addition to the color-forming groups, solubilizing groups produced through the medium of aldehydoacids are frequently present. Desirably, from 0.1% to 5% of the hydroxyls are acetalized in order to give a suitable degree of water or alkali solubility.

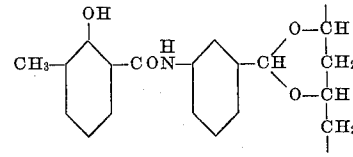
As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. A photographic element comprising a support bearing a water-permeable silver halide emulsion layer having in contact with the silver halide grains a polymeric acetal of a hydroxyl polymer which contains a plurality of recurring intralinear



polymer unit groups and groups of the formula:

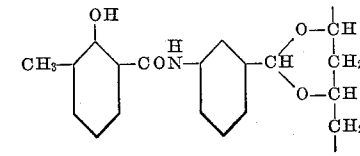


2. A photographic element comprising a support bearing a water-permeable silver halide emulsion layer having in contact with the silver halide grains an acetal of polyvinyl alcohol with m-(3-methylsalicylamido) benzaldehyde in which 0.75 to 7.5% of the hydroxyl groups of the polyvinyl alcohol are acetalized with said aldehyde.

3. A photographic element comprising a support bearing a water-permeable silver halide emulsion layer having in contact with the silver halide grains an acetal of polyvinyl alcohol with m-(3-methylsalicylamido) benzaldehyde in which 0.75 to 7.5% of the hydroxyl groups of the polyvinyl alcohol are acetalized with said aldehyde, and 0.1 to 5.0% are acetalized with sodium o-benzaldehyde sulfonate.

4. A photographic element comprising a support bearing a layer consisting of light-sensitive silver halides which are dispersed in a polymeric acetal of a hydroxyl polymer which contains a plurality of recurring intralinear

polymer unit groups and groups of the formula:



5. A photographic element comprising a support bearing a layer consisting of light-sensitive silver halides which are dispersed in an acetal of polyvinyl alcohol with m-(3-methylsalicylamido) benzaldehyde in which 0.75 to 7.5% of the hydroxyl groups of the polyvinyl alcohol are acetalized with said aldehyde.

6. A photographic element comprising a support bearing a layer consisting of light-sensitive silver halides which are dispersed in an acetal of polyvinyl alcohol with m-(3-methylsalicylamido) benzaldehyde in which 0.75 to 7.5% of the hydroxyl groups of the polyvinyl alcohol are acetalized with said aldehyde, and 0.1 to 5.0% are acetalized with sodium o-benzaldehyde sulfonate.

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REFERENCES CITED

The following references are of record in the file of this patent:

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