

1

3,003,879

NONAQUEOUS PHOTOGRAPHIC EMULSIONS

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This invention relates to photographic emulsions, the liquid portion of which is an organic solvent and the carrier for the silver halide is a carboxylated polyvinyl acetal or butyral, the salts of which are soluble in water and the acid forms of which are soluble in certain organic solvents.

Photographic emulsions are usually prepared by precipitating silver halide grains in an aqueous solution of a peptizer, such as a water-soluble synthetic polymer like polyvinyl alcohol. Often the resulting silver halide is subjected to a series of operations to promote grain growth and to remove the potassium nitrate formed during the silver halide precipitation, after which the grains are dispersed in an aqueous solution of a vehicle prior to coating on a film base.

In the case of special applications such as for facilitating the rapid drying of a photographic emulsion upon a support the silver halide and the vehicle therefor has been dispersed in organic solvents. Various polymeric substances have been thought of for vehicles in this connection, but many such materials although soluble in organic solvents are insoluble in water. These polymers would be unsuitable as peptizers for preparing silver halide dispersions inasmuch as the starting materials ordinarily employed i.e. silver nitrate, potassium bromide and potassium iodide are generally insoluble in organic solvents. Hydrophobic water-insoluble polymers do not swell appreciably in water and, hence, offer resistance to penetration by aqueous solutions. Emulsion coatings prepared from such polymers would be resistant to penetration by aqueous photographic developer and fixer solutions. Some polymers which are soluble both in water and organic solvents do not readily lend themselves to washing out of the soluble salts (formed in the preparation of the silver halide) by a temporary coagulation of the silver halide grains.

One object of our invention is to provide nonaqueous photographic emulsions in which the carrier for the silver halide is a carboxylated polyvinyl acetal or carboxylated polyvinyl butyral, which is water soluble in the salt form and soluble in certain organic solvents in the free-acid form. Another object of our invention is to provide a procedure for the preparation of nonaqueous photographic emulsions in which the polymer employed as the peptizer for the silver halide may correspond to that which is employed as the protective colloid in the nonaqueous emulsion which is ultimately formed. Other objects of our invention will appear herein.

We have found that nonaqueous photographic emulsions can be conveniently prepared by means of carboxylated polyvinyl acetals or carboxylated polyvinyl butyrals containing at least 2 mole percent of carboxyl by preparing the silver halide dispersion in water solution using the salt form thereof and from this preparing the emulsion proper using the free-acid form of the polymer which is soluble in organic solvent. We have found that

2

after the silver halide dispersion has been formed using the salt form of the polymer, the dispersion may be coagulated and the grains thus obtained may be dried without any interference with their dispersion in organic solvents. The nonaqueous photographic emulsions in accordance with our invention may be prepared using either dioxane, isopropanol, acetone or dimethoxyethane as the liquid portion of the emulsion. In the use of the carboxylated polyvinyl acetals the material employed should contain 60-87 mole percent of polyvinyl acetal and at least 4 mole percent carboxyl should be present therein. In the case of the carboxylated polyvinyl butyrals there should be 50-75 mole percent of polyvinyl butyral and the minimum carboxyl content should be 4 mole percent if the polyvinyl butyral content is 50%, and 17 mole percent if the polyvinyl butyral content is in the vicinity of 75%. The preparation of carboxylated polyvinyl acetals and butyrals may be in accordance with the method described in U.S. Patent No. 2,828,289 of John W. Mench.

The nonaqueous emulsions in accordance with our invention are prepared by first preparing an aqueous dispersion of silver halide in an aqueous solution of a water soluble salt of carboxylated polyvinyl acetal or butyral. After the dispersion has formed, the silver halide grains are coagulated by the addition of acid to reduce to a pH within the range of 3-4.5. The coagulum thus formed is separated from the liquid and is preferably washed, such as with distilled water and is dried. The coagulum is then dispersed in an organic liquid containing in solution the free acid form of carboxylated polyvinyl acetal or butyral. If desired, in the preparation of the emulsion, ripening of the silver halide grains may be employed and sensitizers or other additives may be added to the emulsion composition. For instance, if desired, a hardener such as bis(2,3-epoxypropoxyethyl)ether may be incorporated in an amount of 4% based on the weight of the polymer. Any suitable hardener, however, may be added to the composition. Instead of dispersing the silver halide in a solution of carboxylated polyvinyl acetal or butyral it may be incorporated in a solution of a mixture of one of those materials with a polyvinylacetal providing 1/2 or more of the polymer is the carboxylated product. In cases where permeability of the emulsion layer is not critical even a higher proportion of the polyvinyl acetal may be used.

The carboxylated polyvinyl acetal or carboxylated polyvinyl butyral may be prepared by reacting upon a polyvinyl acetal or butyral with any dicarboxylic acid preferably in the form of its anhydride. Although the phthaloylated material has been found to be quite useful other dicarboxylic acid groups such as succinyl, maleyl, diglycolyl or the like might be incorporated in the polyvinyl compound such as by reacting the polyvinyl compound with the corresponding anhydride. The nonaqueous photographic emulsions obtained in accordance with our invention may be coated on to a suitable support forming layers which are characterized by being permeable to aqueous alkaline photographic processing solutions that convert the polymer vehicle to the hydrophilic water permeable form. The polymer which is employed as the carrier for the silver halide should be present in the emulsion in an amount at least equal to the amount of the silver halide which is present therein. The mere use of carboxylated polyvinyl acetal in an amount only

3

sufficient to act as a color former in the emulsion does not serve as the vehicle for the silver halide in the non-aqueous photographic emulsion.

The following examples illustrate our invention:

Example 1

Two solutions were prepared as follows:

- A. 14.1 ml. of 2 molar silver nitrate
2.2 ml. of ammonium hydroxide (specific gravity 10.90)
13.7 ml. of water at a temperature of 17° C.
- B. 1.6 grams of the ammonium salt of phthaloylated polyvinyl acetal containing 72.5 mole percent of polyvinyl acetal, 21.9 mole percent of polyvinyl alcohol, and 5.6 mole percent of polyvinyl phthalate
31.4 ml. of water
16.6 ml. 2 molar potassium bromide
0.8 ml. of 0.5 molar potassium iodide
Temperature: 17° C.

Solution A was run into solution B over a period of approximately 2 minutes, solution B having been stirred continuously. A silver halide dispersion was obtained. The silver halide grains therein were coagulated by the addition of 100 ml. of 20% aqueous acetic acid to the dispersion. The coagulum which formed was separated from the liquid portion and was washed by 3 consecutive washes each with 1 liter of distilled water following which the coagulum was dried at 65° C. for 18 hours. The dried coagulum was suspended in 23.6 grams of dioxane with heating and stirring. This suspension was then dispersed in 76.4 grams of a 7% solution in dioxane of the free-acid form of a phthalated polyvinyl acetal described under B above. The emulsion was coated onto cellulose triacetate film base at 19° C., and the coating thus formed was dried by the application of warm dry air. The emulsion coating was permeable to alkaline photographic developer and fixer solutions.

Example 2

Emulsion making procedure as described in Example 1 was followed except that isopropanol was used as the organic solvent and the polymeric peptizer and vehicle was the salt and free-acid form respectively of a phthaloylated polyvinyl butyral containing 50.0 mole percent polyvinyl butyral, 38.3 mole percent polyvinyl alcohol, 7.5 mole percent polyvinyl phthalate, and 4.2 mole percent polyvinyl acetate, and solutions A and B were kept at 26° C. instead of 17° C. The emulsion was coated onto a cellulose triacetate film base and the coating was dried by a current of warm dry air. It was found to be permeable to alkaline photographic developer and fixer solutions.

Example 3

Emulsion making procedure as described in Example 1 was followed except that acetone was used as the organic solvent and the polymeric peptizer and vehicle was the salt and free-acid form respectively of a copolymer containing 75 mole percent ethyl acrylate and 25 mole percent acrylic acid and solutions A and B were kept at 26° C. instead of 17° C. The emulsion was coated onto a polyethylene terephthalate film base and the coating was dried by a current of warm dry air. It was found to be permeable to alkaline photographic developer and fixer solutions.

Coatings prepared from organic solvent solutions of the free-acid form of carboxylated polyvinyl acetal or butyral differ from coatings prepared from aqueous solutions of salts of those polymers in that they show lower swelling values in photographic processing solutions and lower regain values at higher relative humidity. For instance, a coating prepared from a dioxane solution of

4

the free-acid form of phthalated polyvinyl acetal was compared with a coating prepared from an aqueous solution of the ammonium salt of phthaloylated polyvinyl acetal. The following values were obtained:

Swelling in Kodak DK-50 developer (5 minutes immersion)	Swelling in Kodak F-24 fixer diluted with an equal amount of water, pH adjusted to 9.1 (5 minutes immersion following the 5 minutes immersion in DK-50 developer and 15 seconds immersion in 3% acetic acid solution)	Regain at 25° C., 78% R.H.
	Percent	Percent
Coating from dioxane, 200%-----	76	7.05
Coating from water, 274%--	116	9.93

The flex life and abrasion resistance of coatings of the nonaqueous photographic emulsion coatings were equivalent to those from coatings made from the aqueous solution.

Some of the materials described herein are useful as vehicles for aqueous silver halide photographic emulsions. Thus, aqueous dispersions of carboxylated polyvinyl acetals containing 60 to 87 mole percent of polyvinyl acetal and 1 to 12 mole percent of polyvinyl phthalate gel as the temperature is raised, which facilitates rapid high temperature drying. When the polyvinyl acetal concentration is at the low end of range, e.g., 60 mole percent, the polyvinyl phthalate content must be held fairly critically between 2 and 4 mole percent to insure useful heat gelling properties; at the high end, e.g., around 87 mole percent, the polyvinyl phthalate concentration can vary considerably, say from 2 to 12 mole percent.

Representative compositions are tabulated below:

MOLE PERCENT CONCENTRATIONS IN TYPICAL HEAT SETTING CARBOXYLATED POLY-VINYL ACETALS

Vinyl alcohol units	Vinyl acetal units	Vinyl phthalate units
33-36	60	2-4
23-16	75	2-9
11-1	87	2-12

The photographic emulsions used in practicing our invention are of the developing-out type.

The emulsions can be chemically sensitized with sulfur compounds such as those described in Sheppard U.S. Patent 1,574,944; Sheppard and Punnett U.S. Patent 1,623,499; and Sheppard and Brigham U.S. Patent 2,410,689.

The emulsions can also be treated with salts of the noble metals such as ruthenium, rhodium, palladium, iridium, and platinum. Representative compounds are ammonium chloropalladate, potassium chloroplatinate, and sodium chloropalladate, which are used for sensitizing in amounts below that which produces any substantial fog inhibition, as described in Smith and Trivelli U.S. Patent 2,448,060, and as antifoggants in higher amounts, as described in Trivelli and Smith U.S. Patents 2,566,245 and 2,566,263.

The emulsions can also be chemically sensitized with gold salts as described in Waller, Collins, and Dodd U.S. Patent 2,399,083 or stabilized with gold salts as described in Damschroder U.S. Patent 2,597,856 and Yutzy and Leermakers U.S. Patent 2,597,915. Suitable compounds are potassium chloroaurite, potassium aurithiocyanate, potassium chloroaurate, auric trichloride and 2-auriosulfobenzothiazole methochloride.

The emulsions can also be chemically sensitized with reducing agents such as stannous salts (Carroll, U.S. Patent 2,487,850), polyamines, such as diethylene triamine (Lowe and Jones, U.S. Patent 2,518,698), polyamines, such as spermine (Lowe and Allen, U.S. Patent

5

2,521,925), or bis(β -aminoethyl)sulfide and its water-soluble salts (Lowe and Jones, U.S. Patent 2,521,926).

The emulsions can also be optically sensitized with cyanine and merocyanine dyes, such as those described in Brooker U.S. Patents 1,846,301; 1,846,302; and 1,942,854; White U.S. Patent 1,990,507; Brooker and White U.S. Patents 2,112,140; 2,165,338; 2,493,747; and 2,739,964; Brooker and Keyes U.S. Patent 2,493,748; Sprague U.S. Patents 2,503,776 and 2,519,001; Heseltine and Brooker U.S. Patent 2,666,761; Heseltine U.S. Patent 2,734,900; Van Lare U.S. Patent 2,739,149; and Kodak Limited British Patent 450,958.

The emulsions can also be stabilized with the mercury compounds of Allen, Byers, and Murray U.S. Patent 2,728,663; Carroll and Murray U.S. Patent 2,728,664; and Leubner and Murray U.S. Patent 2,728,665; the triazoles of Heimbach and Kelly U.S. Patent 2,444,608; the azaindenes of Heimbach and Kelly U.S. Patents 2,444,605 and 2,444,606; Heimbach U.S. Patents 2,444,607 and 2,450,397; Heimbach and Clark U.S. Patent 2,444,609; Allen and Reynolds U.S. Patents 2,713,541 and 2,743,181; Carroll and Beach U.S. Patent 2,716,062; Allen and Beifuss U.S. Patent 2,735,769; Reynolds and Sagal U.S. Patent 2,756,147; Allen and Sagura U.S. Patent 2,772,164, and those disclosed by Birr in the Z. wiss. Phot. 47, 2 (1952); the disulfides of Belgian Patent 569,317; the quaternary benzothiazolium compounds of Brooker and Staud U.S. Patent 2,131,038 or Allen and Wilson U.S. Patent 2,694,716 (e.g., decamethylene-bis-benzothiazolium perchlorate); and the zinc and cadmium salts of Jones U.S. Patent application Serial No. 493,047.

The emulsions may also contain speed-increasing compounds of the quaternary ammonium type of Carroll U.S. Patent 2,271,623; Carroll and Allen U.S. Patent 2,288,226; and Carroll and Spence U.S. Patent 2,334,864; and the polyethylene glycol type of Carroll and Beach U.S. Patent 2,708,162.

In the preparation of our emulsions various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromiodide. The emulsion vehicles described herein may be used in emulsions intended for color photography, for example, emulsions containing color-forming couplers or emulsions to be developed by solutions containing couplers or other color-generating materials, emulsions of the mixed-packet type, such as described in Godowsky U.S. Patent 2,698,794 or emulsions of the mixed-grain type, such as described in Carroll and Hanson U.S. Patent 2,592,243. The vehicles can also be used in emulsions which form latent images predominantly on the surface of the silver halide crystal or in emulsions which form latent images predominantly inside the silver halide crystal, such as those described in Davey and Knott U.S. Patent 2,592,250.

The vehicles may also be used in emulsions intended for use in diffusion transfer processes which utilize the undeveloped silver halide in the nonimage areas of the negative to form a positive by dissolving the undeveloped silver halide and precipitating it on a receiving layer in close proximity to the original silver halide emulsion layer. Such processes are described in Rott U.S. Patent 2,352,014 and Land U.S. Patents 2,584,029; 2,698,236 and 2,543,181; and Yackel et al. U.S. Patent application Serial No. 586,705. They may also be used in color transfer processes which utilize the diffusion transfer of an image-wise distribution of developer, coupler or dye, from a light-sensitive layer to a second layer, while the two layers are in close proximity to one another. Color processes of this type are described in Land U.S. Patents 2,559,643 and 2,698,798; Land and Rogers Belgian Patents 554,933 and 554,934; International Polaroid Belgian Patents 554,212 and 554,935; Yutzky U.S. Patent 2,756,142, and Whitmore and Mader U.S. Patent application Serial No. 734,141.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions there may

6

be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound.

Combinations of these antifoggants, sensitizers, etc., may be used.

We claim:

1. A method of making nonaqueous photographic emulsions which comprises reacting silver nitrate and water soluble halide in an aqueous solution of a peptizer selected from the group consisting of the water soluble salts of carboxylated polyvinyl acetals containing 60-87 mole percent polyvinyl acetal and at least 4 and not more than 40 mole percent of carboxyl, and the water soluble salts of carboxylated polyvinyl butyrals containing 50-75 mole percent polyvinyl butyral, the minimum carboxyl content being within the range of 4-17 mole percent and the maximum carboxyl content being 100 mole percent minus the mole percent of polyvinyl butyral contained therein, coagulating the dispersion thus formed by adjusting the pH to a value within the range of 3-4.5, separating the silver halide coagulum and drying, followed by dispersing the coagulum in a solution of the free acid form of the polyvinyl compound in a solvent selected from the group consisting of dioxane, isopropanol, dimethoxyethane and acetone, whereby a silver halide photographic emulsion composition is obtained.

2. A method of preparing a nonaqueous photographic emulsion which comprises reacting silver nitrate with a water soluble halide in an aqueous solution of a water soluble salt of a carboxylated polyvinyl acetal containing 60-87 mole percent polyvinyl acetal and at least 4 and not more than 40 mole percent of carboxyl, adjusting the pH to a value within the range of 3-4.5 to coagulate the silver halide formed, separating the silver halide coagulum, and drying followed by dispersing the coagulum in a solution of the free acid form of the carboxylated polyvinyl acetal in an organic solvent selected from the groups consisting of dioxane, isopropanol, dimethoxyethane and acetone, whereby a silver halide photographic emulsion is obtained.

3. A method of preparing a nonaqueous photographic emulsion which comprises reacting silver nitrate with a water soluble halide in an aqueous solution of water soluble salt of a carboxylated polyvinyl butyral containing 50-75 mole percent of polyvinyl butyral, the minimum carboxyl content being within the range of 4-17 mole percent and the maximum carboxyl content being 100 mole percent minus the mole percent of polyvinyl butyral contained therein, whereby a silver halide dispersion is formed, adjusting to a pH of 3-4.5 whereby the silver halide is coagulated, separating the resulting coagulum from the liquid portion of the mass, and drying followed by dispersing the coagulum in a solution of the free acid form of the carboxylated polyvinyl butyral in an organic solvent selected from the group consisting of dioxane, isopropanol, dimethoxyethane and acetone, whereby a silver halide photographic emulsion is obtained.

4. A method of preparing a nonaqueous photographic emulsion which comprises reacting silver nitrate with a water soluble halide in an aqueous solution of an ammonium salt of phthaloylated polyvinyl acetal containing 60-87 mole percent polyvinyl acetal and at least 4 and not more than 40 mole percent of carboxyl, coagulating the silver halide grains thus formed by adjusting to a pH within the range of 3-4.5 separating the thus formed coagulum, washing and drying and dispersing the coagulum in a solution of the free acid form of the phthaloylated polyvinyl acetal in dioxane, whereby a silver halide photographic emulsion is obtained.

5. A method of preparing a nonaqueous photographic emulsion which comprises reacting silver nitrate with a water soluble halide in an aqueous solution of the ammonium salt of phthaloylated polyvinyl butyral contain-

ing 50-75 mole percent polyvinyl butyral, the minimum carboxyl content being within the range of 4-17 mole percent and the maximum carboxyl content being 100 mole percent minus the mole percent of polyvinyl butyral, coagulating the silver halide grains thus formed by adjusting to a pH within the range of 3-4.5, separating the thus formed coagulum, washing and drying and dispersing the coagulum in a solution of the free acid form of phthaloylated polyvinyl butyral in isopro-

5

panol whereby a silver halide photographic emulsion is obtained.

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