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PHOTOGRAPHIC ELEMENTS

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This invention relates to photography. More particularly it relates to water permeable colloid layers of photographic elements. Still more particularly, it relates to photographic elements which contain at least one water-permeable layer composed of a hydrolyzed aliphatic mono-olefin/vinyl ester interpolymers, said elements containing at least one stratum of a light-sensitive silver salt.

Since the earliest days of photography, research has been constantly directed towards improving photographic emulsions. Collodion was one of the first materials used as a binder for the light-sensitive silver halides. Collodion, however, has a great many disadvantages because of its low permeability to aqueous solutions. In addition, special methods of dispersion must be used and only emulsions of low speed can be obtained. Gelatin was adopted as a binder for the light-sensitive silver halides many years ago and is still used in practically all commercial photographic film. Although gelatin is much more satisfactory than collodion, it possesses a number of disadvantages. Among these may be cited its sensitivity to bacterial decomposition, low stability to heat, extreme brittleness, particularly when dry and in the cold, non-uniformity from batch to batch, and limited range of processing temperatures. Albumin, agar-agar, casein, and cellulose derivatives have also been tried as emulsion binders but are less satisfactory than gelatin. Recently it has been proposed to employ certain polyvinyl alcohol derivatives in conjunction with special dispersing and gelling agents as gelatin substitutes, but they are inferior in many respects to gelatin.

It is an object of this invention to provide new and useful photographic emulsions. A further object is to provide photographic emulsions which are superior to gelatin emulsions. A still further object is to provide photographic emulsions which are uniform, stable, resistant to bacteria, and form layers which are flexible over a wide range of temperatures. A further object is to provide novel photographic elements with layers containing colloid layers superior to gelatin layers. Still other objects will be apparent from the following description of the invention.

The above objects are attained and new and useful photographic elements provided by the preparation and use of photographic elements which comprise a support bearing at least one layer composed of a hydrophilic hydrolyzed mono-olefin/vinyl ester interpolymers. The hydrophilic interpolymers are dissolved in a solvent,

e. g., water containing 10% of a water soluble polar solvent such as methyl alcohol, ethyl alcohol, isopropyl alcohol or the like, admixed with a chemical component of a photographic element such as a light-sensitive material, pigment, dye, dye intermediate, color former, or antihalation material, etc., coated onto a support or base or a water permeable colloid layer imposed thereon, and dried. The coating may be accomplished in the same manner that gelatino-silver halide emulsions, filter layers, antihalation layers, anti-abrasion layers, etc., are coated onto such supports.

A preferred aspect of the invention is concerned with photographic elements containing at least one light-sensitive silver halide colloid layer wherein the colloid is a hydrophilic, completely hydrolyzed ethylene/vinyl acetate interpolymers which has a low ethylene content. In the preferred aspect of the invention ethylene/vinyl acetate interpolymers prepared as described below and more fully in application Serial No. 446,116, filed June 6, 1942, are completely hydrolyzed and utilized as the starting materials for the present invention. The hydrophilic hydrolyzed polymer is dissolved in water containing from 5 to 20% of ethanol, a water soluble inorganic halide is dissolved in the aqueous solution of the polymer, and a solution of silver nitrate or other soluble silver salt is added to this solution with stirring. The emulsion may then be further treated, e. g., ripened, freed from excess soluble salts, digested, and/or modified by addition of further interpolymers, sensitizers, anti-fogging agents, preservatives or hardeners, etc.

It has been found advantageous after precipitating the silver halide in the solution and ripening, to remove soluble salts by precipitating the emulsion by addition of acetone or an inorganic salt, such as sodium sulfate, whereupon particles of the hydrolyzed ethylene/vinyl acetate interpolymers containing silver halide dispersed therein are precipitated. The supernatant liquid is removed, and the emulsion particles are washed in water. The resulting washed, light-sensitive emulsion is then dissolved by heating with water, preferably with the addition of a small amount of alcohol, and after digestion is coated upon a suitable support, such as paper, metal, glass, or a transparent cellulose derivative film, e. g., nitrocellulose, cellulose acetate, cellulose acetate propionate; or a synthetic resin or superpolymer, e. g., nylon, polyvinyl acetals, etc. After drying, the resulting light-sensitive film element can be used in the same manner as photographic ele-

ments containing gelatin/silver halide layers. For example, after exposure, the element bearing the latent image is developed in a standard p-methylaminophenol/hydroquinone - type developer at a temperature of 18 to 35° C. and fixed in an acid hypo bath. The resulting negative is of good contrast and quality and can be further processed in the same way as the conventional photographic elements with gelatin layers.

The hydrophilic hydrolyzed olefin/vinyl ester interpolymers can be used in light-sensitive film elements in ways other than as binder for the light-sensitive material; for example, they may be used as a water-permeable colloid in layers containing no light-sensitive material as, for example, in filter layers, anti-static layers, anti-abrasion coatings, and anti-halation and daylight-loading backings, or in layers which contain a dye or dye intermediate or color former and coat with a light-sensitive silver halide layer to form dye images on bleaching of a silver image or development of a silver salt image, respectively.

The materials used in the water-permeable colloid layers of the photographic elements of this invention are hydrolyzed mono-olefin/vinyl ester interpolymers having hydrophilic properties. These are suitably prepared by polymerizing the vinyl ester and an aliphatic monoolefinic hydrocarbon of 2 to 4 carbon atoms containing a double bond between a terminal carbon atom and the vicinal carbon atom, with a persulfate or peroxide-type catalyst under moderate pressures at temperatures of 50-80° C. followed by hydrolysis in acid or basic aqueous solutions. Any hydrolyzable, polymerizable vinyl ester of an organic acid can be used as far as is known. The vinyl esters of the lower fatty acids such as vinyl acetate or vinyl propionate are preferred by virtue of their availability, ease of copolymerization, ease of hydrolysis, and low cost.

Suitable hydrolyzed ethylene/vinyl ester interpolymers can be made from the ethylene/vinyl acetate interpolymers described in application Serial No. 446,116, filed June 6, 1942.

Hydrolysis or alcoholysis of the ethylene/vinyl ester interpolymers of aforesaid application and related interpolymers is preferably carried out by dissolving the interpolymer in an alcohol such as methanol or ethanol, or in a mixture of an alcohol and a hydrocarbon such as toluene, and then treating with a suitable hydrolyzing agent or catalyst such as an alkali, e. g., NaOH, KOH, or an acid, e. g., HCl, H₂SO₄, p-toluenesulfonic acid, etc. The hydrolysis may be partial or complete, depending on the nature of the solvent, the amount and kind of catalyst used, and the time and temperature of reaction. The following general principles apply: (1) the greater the amount of vinyl ester in the interpolymer, the more rapid the rate of hydrolysis; (2) alkali hydrolyzing agents give more rapid hydrolysis than mineral acid catalysts.

The term "hydrolysis" as used herein and in the accompanying claims is intended to include alcoholysis as well as hydrolysis with the use of water. Regardless of whether water or an alcohol is used to split off the ester groups in the interpolymer, the product is the same.

Complete hydrolysis can be obtained in most cases by dissolving the interpolymer in alcohol or alcohol-toluene to give about 10% solution, adding an excess of sodium or potassium hydroxide in alcohol and refluxing for about one hour.

The useful hydrophilic interpolymers may be further characterized as hydrolyzed interpoly-

mers of aliphatic, terminally-unsaturated mono-olefins and vinyl esters containing these ingredients in mol ratio of 0.3 to 0.02 of olefin to 1.0 of hydrolyzed vinyl ester, which are water permeable and soluble in water at 80° C. or in water-ethanol mixtures containing 10% of the latter. When the olefin is isobutylene this corresponds to an olefin content of 27% to 2.4% by weight in the hydrolyzed polymer. When the olefin is ethylene this corresponds to an ethylene content of 16% to 1.2% by weight. In general hydrolyzed interpolymers containing 10% or less of the olefin by weight are preferred because of their greater permeability to photographic processing solutions. However, it has been found that a polymer containing as little as one mol of ethylene combined with 45 mols of vinyl acetate, as determined by carbon analysis, gives a satisfactory product upon hydrolysis. The small proportion of ethylene or other olefin renders the products different from polyvinyl alcohol and hydrolyzed polyvinyl esters which are very sensitive to water and aqueous photographic processes. Films of polyvinyl alcohol are readily dissolved away from their supports upon contact with water, photographic developers, dilute acid, fixing solutions, and the like, whereas the present interpolymers are not. In addition polyvinyl alcohol films show undesirably high swelling in water and become tacky more readily than the hydrolyzed olefin/vinyl ester interpolymers of the present invention. This means polyvinyl alcohol cannot be handled easily in photographic applications. Attempts have been made to improve the performance of polyvinyl alcohol by modifying it with gelling agents, by partial acetalization, by hardening with zirconium salts, by incomplete saponification of the original polyvinyl acetate, and the like which are unnecessary with the present products.

The difference in water sensitivity between polyvinyl alcohol and the interpolymers of the present invention is shown in the following table in which the tensile strengths of films are compared after soaking in water at 25° C. for 15 min.

Polymer	Wet tensile strength, lb./in. ²
Polyvinyl alcohol (completely hydrolyzed)	0
Completely hydrolyzed ethylene/vinyl acetate interpolymer containing 2.6% ethylene by weight	1820
Hydrolyzed polyvinyl acetate containing 10% acetate groups	0

The method of hydrolysis of the olefin-vinyl ester interpolymers appears to be of little importance, provided adequate precautions are taken to insure that the polymer is not contaminated by impurities which adversely affect photographic properties. It is to be understood that the term "hydrolysis" is used herein in its broad sense, including alcoholysis. The degree of hydrolysis, however, when considered in conjunction with the mol ratio of the interpolymer, determines whether or not a satisfactory product is obtained. It has been found that polymers hydrolyzed only partially, e. g., 85-95%, are more water-sensitive than the completely hydrolyzed polymers. For this reason, a polymer having an olefin/vinyl ester mol ratio greater than 0.3 can sometimes be adjusted to produce a satisfactory product by hydrolyzing only partially. On the other hand, polymers with very low proportions of olefin should be hydrolyzed completely in order to obtain maximum permeability without too great

ease of solution. The preferred elements of this invention utilize interpolymers having an olefin/vinyl ester mol ratio of less than 0.2 which are completely hydrolyzed.

The invention will be further illustrated but is not intended to be limited by the following examples wherein the parts stated are parts by weight.

Example I

An ammoniacal silver nitrate solution is prepared by adding concentrated ammonium hydroxide to 20 parts of an aqueous solution containing 11 parts of silver nitrate until the precipitate of silver hydroxide disappears. Two parts of a 1% aqueous sodium dodecyl sulfate solution is then added. The resulting "converted" silver nitrate solution and a solution of 6.6 parts of ammonium bromide, 0.3 part of potassium iodide and 0.02 parts of sodium dodecyl sulfate in approximately 30 parts of water are added simultaneously in fine streams to a stirred solution of 4 parts of completely hydrolyzed ethylene/vinyl acetate polymer having a mol ratio of 0.07 of ethylene to 1.0 of vinyl acetate in the original interpolymers in 32 parts of water and 4 parts of ethanol. The temperature is held at 45° C. during the precipitation and for a period of 15-60 minutes after completion thereof. The silver halide emulsion is coagulated by running in a fine stream of acetone (300-400 parts) at room temperature. The coagulate is then washed 6 times with fresh portions of water (400 parts) at 10-minute intervals. The washed emulsion is dissolved by stirring at 60° C. for 15-60 minutes with 10 parts of ethanol and 40 parts of a 10% solution of the original completely hydrolyzed interpolymers of ethylene/vinyl acetate of mol ratio 0.07 in water containing 11% ethanol. The emulsions are coated on heavy white baryta-coated paper and dried in warm dry air.

A negative picture is printed by projection onto the silver bromide printing paper just described and then developed in the following solution:

Water	parts..	500
p-Methylamino-phenol sulfate.....	do.....	3
Anhydrous sodium sulfite.....	do.....	45
Hydroquinone	do.....	12
Anhydrous sodium carbonate.....	do.....	67.5
Potassium bromide.....	do.....	1.9
Add water to make.....	cc.....	1000

After development at 18-30° C. for 1-3 minutes, the film is fixed in the normal way in a 25% sodium thiosulfate bath containing approximately 1% of sodium bisulfite, washed and dried. It can be processed at a temperature of 50° C. without causing reticulation. The resulting picture is in the form of a black silver image of good gradation and clarity.

Example II

A solution of 5 parts of completely hydrolyzed ethylene/vinyl acetate polymer of mol ratio 0.04 (prepared by interpolymers of ethylene and vinyl acetate as described in Example V, Serial No. 446,116, followed by alkali-catalyzed methanolysis as described in Example XI, Serial No. 446,114, continuation application Serial No. 577,736 filed February 13, 1945, now United States Patent 2,386,347) is mixed with 7 parts of ammonium bromide in 25 parts of water at 40° C. To this solution is added with stirring at 40° C. 11 parts of silver nitrate in 20 parts of water. After a suitable ripening period at this temperature (15-16 minutes) the photographic emulsion is

coated on paper and allowed to dry. The resulting photographic element may be exposed and processed in a manner as described in Example I.

Example III

A solution of ammoniacal silver nitrate is prepared as in Example I from 11 parts of silver nitrate, 30 parts of water, and sufficient ammonium hydroxide to produce a clear solution. This solution and one containing 10 parts of potassium bromide and 0.1 part of potassium iodide in 40 parts of water are added simultaneously at 45° C. to a stirred mixture of 4 parts of completely hydrolyzed ethylene/vinyl acetate polymer (mol ratio of 0.12 of ethylene to 1.0 of vinyl acetate), 15 parts of ethanol, and 60 parts of water. The resulting emulsion is stirred for 5 minutes, coagulated with an excess of acetone, and washed as in Example I. The washed material is dissolved in a mixture of 4 parts of completely hydrolyzed ethylene/vinyl acetate interpolymers (mol ratio of 0.12 of ethylene to 1.0 of vinyl acetate) in 20 parts of water and 20 parts of ethanol by stirring at 60° C. for 10 minutes. When the resulting emulsion is coated on heavy white baryta paper, dried, and processed as in Example I, a black silver image of comparable quality is obtained.

Example III-A

A solution consisting of 90 parts of silver nitrate and 900 parts of water and 100 parts of ammonium hydroxide is added with stirring to a mixture of 55 parts of ammonium bromide and 1 part of potassium iodide dissolved in a solution of 35 parts of completely hydrolyzed ethylene/vinyl acetate polymer of the type described in Example II in 480 parts of water and 35 parts of ethanol. The mixture thus obtained is stirred at 40° C. for one hour, then coagulated by adding 700 to 1000 parts of a 10% aqueous solution of sodium sulfate with rapid stirring. The coagulate in the form of curds or particles is freed of soluble salts by washing with a continuous stream of water for 1-2 hours. Excess water is separated by decantation and to the coagulate is added 35 parts of hydrolyzed ethylene/vinyl acetate polymer (described above) in 300 parts of 10% ethanol and 500 parts of water. After digesting at 65° C. for 30 minutes, the photographic emulsion is coated on a baryta sized paper and dried. It is exposed to a negative image by projection printing and processed as in Examples I and III whereby a black silver positive image of excellent quality is obtained.

Example IV

The hydrolyzed ethylene/vinyl acetate polymer of Example I is replaced by completely hydrolyzed propylene/vinyl acetate interpolymers of mol ratio of 0.07 of propylene to 1.0 vinyl acetate and a light-sensitive emulsion is prepared as in Example I. When the emulsion is coated on heavy white baryta paper and processed as in Example I, a black silver image of good gradation is obtained.

Example V

The hydrolyzed ethylene/vinyl acetate interpolymers of Example I is replaced by completely hydrolyzed isobutylene/vinyl acetate polymer of mol ratio of less than 0.2 of isobutylene to 1.0 vinyl acetate and an emulsion is prepared in the same manner using solutions containing 4 parts of completely hydrolyzed isobutylene/vinyl acetate polymer in 32 parts of water and 8 parts of ethanol. The emulsion is coated and processed

as in Example I, and an image of good quality is obtained.

Example VI

A light-sensitive, gelatin-silver halide emulsion prepared in standard fashion is diluted with 4 parts of water at 40° C. and centrifuged to separate the heavy silver halide from the dissolved gelatin. After washing with warm water and re-centrifuging, a dispersion is made from 10 parts of this moist silver halide in 50 parts of water containing 0.5 part of sodium dodecyl sulfate. This silver halide dispersion is added with stirring to 50 parts of a 10% aqueous solution of completely hydrolyzed ethylene/vinyl acetate polymer and 50 parts of water. Then 25 parts of ethyl alcohol is added. The resulting light-sensitive silver halide emulsion is coated and processed as in Example I. It was observed that this light-sensitive layer had the same photographic characteristics as one obtained from a coating of the original silver halide-gelatin emulsion and was much tougher and more resistant to marring upon flexing or scratching.

Example VII

An ortho-sensitized silver iodo-bromide gelatin emulsion containing 1:2-diethylthio- ψ -cyanine is prepared and separated as in Example VI. A dispersion of 4 parts of the centrifuged and washed silver halide grains in 25 parts of water containing 0.25 part of sodium dodecyl sulfate is mixed with a solution of 50 parts of a 10.7% aqueous solution of completely hydrolyzed ethylene/vinyl acetate interpolmer of mol ratio of 0.12 ethylene to 1.0 vinyl acetate and 80 parts of water. To this is added a solution of 1 part of o-sulfobenzylidene-bis (m-stearamidophenylmethyl pyrazolone), (prepared according to the methods described in U. S. P. 2,294,909), dissolved in 30 parts of ethanol and 1 part of 5% sodium hydroxide. The mixture is coated on paper as in Example I or on a cellulose nitrate film base. The coated paper or film, when exposed in a camera or under a transparency, is developed in the following solution:

	Parts
Water.....	980
p-Aminodiethylaniline-hydrochloride	2
Sodium carbonate.....	20
Sodium sulfite.....	2

washed, bleached in 4% potassium ferricyanide, and fixed in 25% hypo to produce a bright magenta-colored picture.

Example VIII

A color-former layer is prepared by coating the following mixture on a gelatin-subbed cellulose acetate film base: 0.8 part of 1-m-aminophenyl-3-methyl-5-pyrazolone, 1 part of 2.5% sodium carbonate solution in 25 parts of water, 40 parts of a 10% solution of a completely hydrolyzed ethylene/vinyl acetate interpolmer, (mol ratio of 0.12 of ethylene to 1.0 of vinyl acetate) in 60 parts of water. A layer of a gelatin-silver halide emulsion of the positive type is coated over the resin layer and the film dried. This film is processed by the method of Example VII to yield a magenta dye image in the interpolmer layer.

Example IX

A mixture containing 10 parts of completely hydrolyzed ethylene/vinyl acetate interpolmer of mol ratio of less than 0.2 of ethylene to 1.0 of vinyl acetate, 10 parts of 5% aqueous saponin

solution, 120 parts of water, and 145 parts of ethanol is coated over a normal X-ray gelatin silver halide emulsion layer at 35° C. This preparation gives a smooth, glossy, flexible layer over the emulsion, furnishing protection from abrasion.

Example X

A solution of 1 part of a 10.7% solution of a completely hydrolyzed ethylene/vinyl acetate polymer of mol ratio of 0.12 of ethylene to 1 of vinyl acetate is mixed with 160 parts of alcohol and 200 parts of water. This is coated on one face of a cellulose nitrate film base which has a light-sensitive gelatin-silver halide layer on the other face. The resulting film is drawn between two insulated rolls and then dropped on an electroscope. It registers a low positive charge which is indicative of a low static film.

Example XI

A solution of 1 part of silver nitrate in 10 parts of water is added with stirring to 50 parts of a 10% solution in aqueous 10% alcohol of a completely hydrolyzed ethylene/vinyl acetate polymer of mol ratio of 0.12 of ethylene to 1 of vinyl acetate and 50 parts of water. A second solution containing 0.3 part of diphenylcarbazine and 0.05 part of ammonium hydroxide in 30 parts of alcohol is added in the same manner, and the resulting mixture is digested at 35° C. for 30 minutes. The yellow, colloidal silver suspension is coagulated, by pouring into acetone, shredded, and washed for 1 hour in a continuous stream of water. The above washed material is then dissolved in a 20:80 ethanol water mixture to obtain a suitable coating viscosity. Modifiers are added to the solution to improve coating uniformity and the material is coated as usual on subbed base. An excellent yellow filter layer is obtained which bleaches readily in alkaline potassium ferricyanide solution.

Example XII

A mixture is made of 50 parts of a 10% aqueous solution of casein, 25 parts of a 10% solution of completely hydrolyzed ethylene/vinyl acetate polymer of mol ratio of 0.12 of ethylene to 1 of vinyl acetate in 10% aqueous ethanol and 10 parts of 5% WSJ Nigrosine (Colour Index No. 865) dye solution. This material is coated over both subbed acetate and nitrate base to give a density of 0.7 to 1.0. The layer can be removed either before development by a gentle swabbing with cotton in water, during development with vigorous agitation or after development by immersion in water.

Example XIII

A film is prepared by coating the emulsion of Example VI on a subbed cellulose acetate film base. On top of this is coated a solution prepared by adding 2 parts of a salicylaldehyde-phthalaldehydic acid acetal of polyvinyl alcohol, as described in U. S. P. 2,310,943, in 10 parts of 5% sodium carbonate solution to 5 parts of completely hydrolyzed ethylene/vinyl acetate interpolmer of mol ratio less than 0.2 of ethylene to 1.0 of vinyl acetate dissolved in 85 parts of water and 10 parts of ethanol. This film, when exposed and processed according to the method of Example VII, yields a blue-green dye image.

Example XIV

The film prepared in Example VI is exposed and developed in the developer of Example VII

to which has previously been added 3 parts of 2-chloroacetoacetanilide. The hydrolyzed ethylene/vinyl acetate interpolymers layer after bleaching in 4% potassium ferricyanide and fixing in 25% hypo contains a yellow dye negative image.

The photographic elements described above can be developed by a reversal process to form satisfactory pictures. Thus, if the film of Examples I to VI are, after the first development and prior to fixing, treated with a chromic acid bath to remove the silver image, then washed, re-exposed to white light, and redeveloped, a reversal image having highlights and densities similar to the original subject are obtained. Similarly, in Examples VII, VIII, XIII, and XIV, if the films are first developed in the developer of Example I, washed, re-exposed to white light, then processed as in the corresponding examples, reversal color images are obtained.

Various types of photographic emulsions utilizing hydrolyzed olefin/vinyl ester interpolymers can be prepared by varying such conditions as temperature, humidity, concentration of reactants, and mode of addition of ingredients. The constituents added to gelatin-silver halide emulsions can be added to the present emulsions including the dyes which modify the optical sensitivity of silver halide emulsions, e. g., the cyanine dyes including carbocyanine, merocyanine, neocyanine, etc., dyes; emulsion sensitizers, e. g., N-allylthiourea, etc.; antifogging agents, pigments, dyes, inorganic salts such as sodium sulfate, sodium thiosulfate, potassium bromide, sodium carbonate, and the like; dispersing or wetting agents, e. g. sodium alkyl sulfates of 10 to 18 carbon atoms, alkyl naphthalene sulfonic acid alkali metal salts, sodium alkyl sulfonates of 10 to 18 carbon atoms, etc.

The good water permeability of the hydrolyzed olefin/vinyl ester interpolymers layers and the fact that they do not dissolve in water at temperatures up to 45° C. makes them useful in additional ways from those described above. For instance, they can be used between the support and a light-sensitive silver halide layer of a photographic element, as an antihalation layer and may contain colloidal silver. They may be used between the silver halide emulsion layers of a film element for multicolor photography in several capacities. For example, they may contain prefogged silver salts which form light barrier layers on development which will enable the layers to be selectively re-exposed and developed to color images. They may be used as barrier layers free from any materials to prevent migration of color formers in silver halide emulsion layers. In the last mentioned types the film elements may contain gelatin-silver halide emulsion layers or hydrolyzed ethylene/vinyl acetate-silver halide layers.

As stated above, the invention is not limited to the use of light-sensitive silver salts such as silver chloride, silver bromide, silver iodide, or mixtures of any of these or mixed crystals containing two or more of such salts in the novel colloid layers. The hydrolyzed ethylene/vinyl acetate interpolymers may contain light-sensitive diazonium salts, dyes, fulgides, dichromates, e. g., ammonium dichromate, etc., or fluorescent materials, e. g. calcium tungstate, lead sulfate, etc.

The interpolymers may be dissolved in hot water, that is, near the boiling point. Upon cooling such solutions, gelation or precipitation normally does not occur, even though the polymer

itself in film form is insoluble in water at room temperature. Thus, it is convenient to coat from an aqueous solution at moderate temperature, and this type of coating can be used to great advantage under certain conditions. It has also been found that aqueous systems containing a small amount of a water-soluble oxygenated organic solvent such as acetone, alcohol, dioxane, acetic acid or methyl acetate are appropriate solvents for the hydrolyzed olefin/vinyl ester interpolymers. Suitable solvents for various applications comprise an aqueous system containing small amounts of a water-soluble aliphatic alcohol such as methanol, ethanol, methoxymethanol, cyclohexanol, benzyl alcohol, furfuryl alcohol, ethanolformamide, propanol, n-butanol, ethylene glycol, glycerol, or the like. The preferred solvent is water containing 0-50% of a water-soluble aliphatic alcohol.

The interpolymers may vary in molecular weight according to the conditions of preparation and, in general, have a molecular weight of 10,000 to 100,000. Interpolymers of molecular weight from 10,000 to 50,000 are preferred.

The ultra-violet transmission of these interpolymers extends down to lower wave lengths than in the case of the ordinary gelatin system, as shown in the following table. This is particularly valuable in X-ray emulsions for use with fluorescent screens which fluoresce strongly in the ultra-violet region:

Solution in ethanol-water	Ultra-violet transmission			
	2900 A.	2800 A.	2600 A.	2400 A.
	Per cent	Per cent	Per cent	Per cent
1% gelatin	43	22	13	0
1% completely hydrolyzed ethylene/vinyl acetate of 0.1 mol ratio ethylene to vinyl acetate	44	42	35	18

A particularly advantageous modification of the present invention lies in the field of color photography. It has been found that the exceptionally clear, colorless, transparent layers obtained with the hydrolyzed olefin/vinyl ester interpolymers lead to less color distortion than with gelatin layers which are non-uniform and yellow in color. In a multilayer color film comprising at least three emulsion layers and composed of the interpolymers hereof, and one or more other layers such as separating or filter layers, the high transmission and freedom from color is of especial advantage in permitting a good balance between the various emulsions. A practical multilayer color film utilizing hydrolyzed olefin/vinyl ester interpolymers in place of the customary gelatin layers may have the following structure:

1. A blue-sensitive emulsion layer comprising silver halide, a hydrolyzed ethylene/vinyl acetate interpolymers as binder, and a yellow color former, for example, p-dodecylacetoacetanilide or N-furoylacet-N'-benzoylacetylbenzidide.

2. A filter layer comprising a dispersion of colloidal silver in hydrolyzed ethylene/vinyl acetate interpolymers as illustrated in Example XI.

3. An orthochromatic emulsion comprising silver halide, a hydrolyzed ethylene/vinyl acetate interpolymers as binder, and a magenta color former, such as the emulsion of Example VII.

4. An emulsion sensitive to blue and red but not to green, comprising silver halide, a hydrolyzed ethylene/vinyl acetate interpolymers as a

binder, and as a blue-green color former, the salicylaldehyde-phthalaldehydic acid acetal of polyvinyl alcohol as described in U. S. P. 2,310,943 or 1-dodecylamino-5-naphthol.

5. A film support such as cellulose acetate or cellulose acetate propionate. The layers imposed thereon are in the order 4, 3, 2, and 1, respectively, with layer 4 being adhesively joined to the support.

The multilayer element just described can be modified by removing the color formers from the respective emulsion layers, as described above, and incorporating them in silver halide-free layers composed of hydrolyzed ethylene/vinyl acetate interpolymers disposed adjacent to the respective emulsions.

The new photographic interpolymer layers may be hardened with such agents as formaldehyde, chromium salts, zirconium salts, aluminum salts, and the like. A method of hardening with polymethylol compounds is also described in application Serial No. 496,460.

The stability of hydrolyzed olefin/vinyl acetate interpolymer emulsions is greatly superior to that of gelatin emulsions. For example, fluid photographic emulsions prepared according to this invention may be stored at room temperature for long periods of time without suffering decomposition. The new film elements of this invention can be advantageously processed at much higher temperatures than has been possible with gelatin. For example, it has been shown possible to process satisfactorily an unhardened film element comprising an emulsion of hydrolyzed ethylene/vinyl acetate interpolymer at a temperature of 50° C. without encountering reticulation. This is of importance in the preparation of emulsions as well as in the processing, since it also permits the use of much higher temperatures in ripening and digestion processes.

Gelatin and other proteins contain the sensitive peptide linkage —CONH— as an integral part of the main polymer chain. In acid, alkali, or hot water the peptide link tends to be hydrolyzed, thus breaking the protein into fragments of lower molecular weight, which are of little value as film-forming materials. The hydrolyzed olefin/vinyl ester interpolymers hereof do not have such disadvantages. They have only carbon-carbon linkages in the main polymer chain and are thus not at all susceptible to such degradation. This is evidenced by their high film strength and good binding properties which are maintained throughout conditions of high temperature and processing in strongly acid or alkaline baths.

A further advantage over gelatin is the fact that the new materials can be obtained with uniform properties, whereas gelatin requires blending to produce a sufficiently uniform product.

Of major importance is the fact that the thin interpolymer layers are tough and flexible as compared with gelatin layers which are brittle. For example, a film of one of the hydrolyzed ethylene/vinyl acetate interpolymers has been shown to flex over 100 times without cracking under conditions of low humidity, whereas a similar gelatin film in the same test cracked on the first bend. This test demonstrates that film elements comprising the hydrolyzed ethylene/vinyl ester interpolymer layers are very much tougher and more resistant to severe handling than the conventional film elements with gelatin layers. This is a decided advantage in the case of cine film, which often breaks due to the embrittling effect of the gelatin layer upon the film base. In con-

junction with a very tough film base, such as polyhexamethyleneadipamide, the provision of a tough, flexible emulsion binder becomes of major importance.

5 The superior qualities of film strength and toughness of the polymeric binders of this invention as compared with gelatin films are very important also from the standpoint of the thickness of the layers of photographic elements. 10 Thus, coating solutions richer in silver halide can be employed and thinner films laid down to produce a photographic element having the required amount of silver halide incorporated in a relatively smaller amount of binder. The thinner 15 layers thus obtained show improvements in definition of the black silver image. These advantages are of especial importance in the multilayer elements used in color photography since the thinner elements give rise to less color distortion than 20 the usual relatively thick gelatin systems.

The light-sensitive film elements of the present invention may be used in general reproduction or copying work, as well as in strictly photographic processes. For example, the materials may be 25 used as a taking stock (negative), as print stock (positive), or as a black and white (or color) reversal film, in the preparation of film for microcopy, e. g., check recording, V-mail, etc., in X-ray films, in lithographic films, in color photography 30 and in portrait materials. In addition, the film elements bearing diazonium salts or ammonium bichromate may be used in the graphic arts and in the reproduction of line drawings.

As many apparently widely different embodiments of this invention may 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 appended claims.

I claim:

40 1. An element for recording photographic images which comprises a support having imposed thereon at least one water-permeable layer composed of a hydrolyzed interpolymer of an aliphatic, terminally unsaturated mono-olefin of 2 45 to 4 carbon atoms and a vinyl ester, said interpolymer having a mol ratio of 0.3 to 0.02 of olefin to 1.0 of vinyl ester and said layer containing a light-sensitive material.

50 2. An element for recording photographic images which comprises a support having imposed thereon at least one water-permeable layer composed of a hydrolyzed ethylene/vinyl acetate interpolymer with a mol ratio of 0.3 to 0.02 of 55 ethylene to 1.0 vinyl acetate containing a light-sensitive material.

3. A photographic element which comprises a support having imposed thereon at least one water-permeable colloid layer composed of a hydrolyzed ethylene/vinyl ester interpolymer having 60 a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl ester, said layer having intimately dispersed therethrough a light-sensitive material.

4. A photographic element which comprises a support having imposed thereon at least one stratum of light-sensitive silver halides dispersed in a completely hydrolyzed ethylene/vinyl ester interpolymer having a mol ratio of 0.2 to 0.02 of 65 ethylene to 1.0 of vinyl ester, said stratum having in operative contact therewith at least one water-permeable colloid layer composed of a completely hydrolyzed ethylene/vinyl ester interpolymer having a mol ratio of 0.2 to 0.02 of ethylene 70 to 1.0 of vinyl ester.

5. A photographic element which comprises a support having imposed thereon at least one stra-

tum of light-sensitive silver halide dispersed in a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said stratum having in operative contact therewith at least one water-permeable colloid layer composed of a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said colloid layer containing a color contributing material taken from the group consisting of pigments, dyes and dye intermediates.

6. A photographic element which comprises a support having imposed thereon at least one stratum of light-sensitive silver halide dispersed in a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said stratum having in operative contact therewith at least one water-permeable colloid layer composed of a completely hydrolyzed ethylene/vinyl acetate interpolymers having mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said colloid layer containing a dye intermediate capable of forming an azo dye upon coupling with a diazo compound.

7. A photographic element comprising a transparent support having a light-sensitive silver halide emulsion layer on one face and an anti-halation layer on the other face thereof each of said layers being composed of a water-permeable hydrolyzed olefin/vinyl ester interpolymers having a mol ratio of 0.3 to 0.02 of olefin to 1 of vinyl ester, said anti-halation layer containing an anti-halation material which is absorptive of certain wave lengths of light to which the emulsion is sensitive.

8. A photographic emulsion comprising a hy-

drolyzed interpolymers of an aliphatic terminally unsaturated mono-olefin of 2 to 4 carbon atoms and a vinyl ester, said polymer having a mol ratio of 0.3 to 0.02 of olefin to 1.0 of vinyl ester and having dispersed therethrough light-sensitive silver salts.

9. A photographic emulsion comprising a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.3 to 0.02 of ethylene to 1.0 of vinyl acetate, having dispersed therethrough light-sensitive silver halides.

10. A photographic emulsion layer composed of a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, having dispersed therethrough light-sensitive silver halides.

11. The process which comprises dissolving a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.3 to 0.02 of ethylene to 1.0 of vinyl acetate in an aqueous solution, precipitating light-sensitive silver halides in the resulting aqueous solution of the interpolymers, coagulating the resulting dispersion, and washing the coagulated interpolymers containing dispersed silver halides with water.

12. The process which comprises dissolving a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.3 to 0.02 of ethylene to 1.0 of vinyl acetate in a water-ethanol mixture containing not more than 50% of ethanol, precipitating light-sensitive silver halides in the resulting solution of the interpolymers, coagulating the resulting dispersion by admixing it with acetone, and washing the coagulated interpolymers containing dispersed silver halides with water.

DAVID M. McQUEEN.

Certificate of Correction

Patent No. 2,397,866.

April 2, 1946.

DAVID M. McQUEEN

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 2, for "bearng" read *bearing*; and second column, line 6, for "containining" read *containing*; page 3, first column, line 75, for "(15-16 minutes)" read *(15-60 minutes)*; page 5, second column, line 35, in the table for "A" all four occurrences, read *A*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of May, A. D. 1946.

[SEAL]

LESLIE FRAZER,

First Assistant Commissioner of Patents.

tum of light-sensitive silver halide dispersed in a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said stratum having in operative contact therewith at least one water-permeable colloid layer composed of a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said colloid layer containing a color contributing material taken from the group consisting of pigments, dyes and dye intermediates.

6. A photographic element which comprises a support having imposed thereon at least one stratum of light-sensitive silver halide dispersed in a completely hydrolyzed ethylene/vinyl acetate interpolymers having a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said stratum having in operative contact therewith at least one water-permeable colloid layer composed of a completely hydrolyzed ethylene/vinyl acetate interpolymers having mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, said colloid layer containing a dye intermediate capable of forming an azo dye upon coupling with a diazo compound.

7. A photographic element comprising a transparent support having a light-sensitive silver halide emulsion layer on one face and an anti-halation layer on the other face thereof each of said layers being composed of a water-permeable hydrolyzed olefin/vinyl ester interpolymers having a mol ratio of 0.3 to 0.02 of olefin to 1 of vinyl ester, said anti-halation layer containing an anti-halation material which is absorptive of certain wave lengths of light to which the emulsion is sensitive.

8. A photographic emulsion comprising a hy-

drolyzed interpolymers of an aliphatic terminally unsaturated mono-olefin of 2 to 4 carbon atoms and a vinyl ester, said polymer having a mol ratio of 0.3 to 0.02 of olefin to 1.0 of vinyl ester and having dispersed therethrough light-sensitive silver salts.

9. A photographic emulsion comprising a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.3 to 0.02 of ethylene to 1.0 of vinyl acetate, having dispersed therethrough light-sensitive silver halides.

10. A photographic emulsion layer composed of a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.2 to 0.02 of ethylene to 1.0 of vinyl acetate, having dispersed therethrough light-sensitive silver halides.

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12. The process which comprises dissolving a hydrolyzed ethylene/vinyl acetate interpolymers with a mol ratio of 0.3 to 0.02 of ethylene to 1.0 of vinyl acetate in a water-ethanol mixture containing not more than 50% of ethanol, precipitating light-sensitive silver halides in the resulting solution of the interpolymers, coagulating the resulting dispersion by admixing it with acetone, and washing the coagulated interpolymers containing dispersed silver halides with water.

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