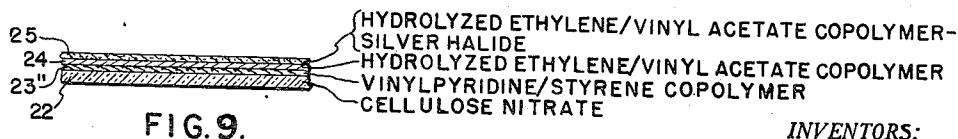
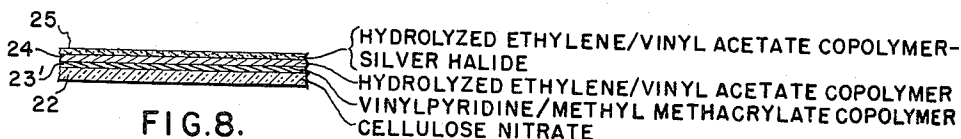
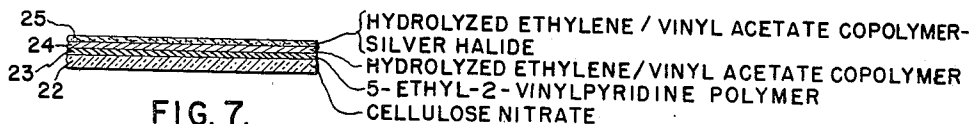
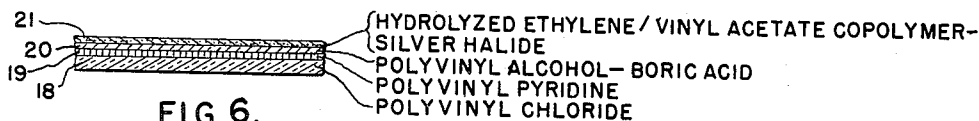
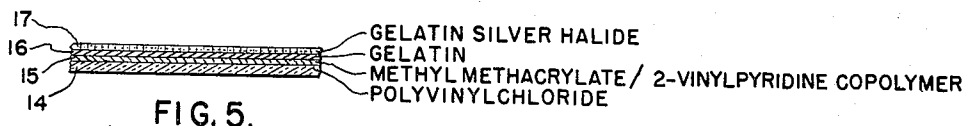
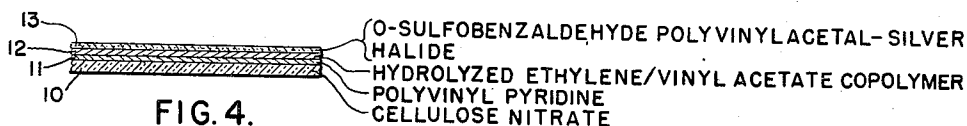
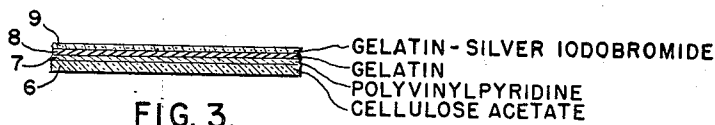
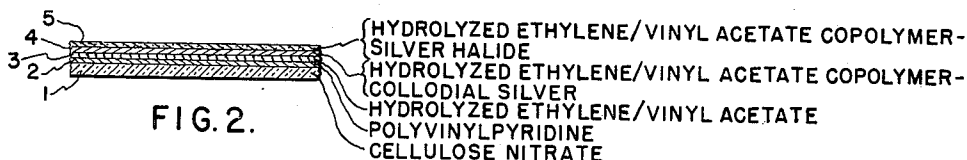
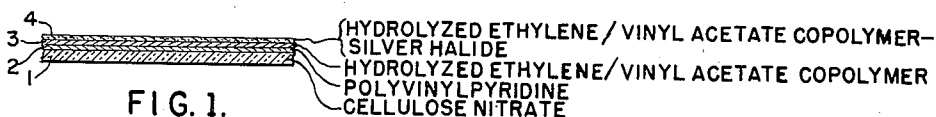


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F. P. ALLES ET AL

2,606,832

PHOTOGRAPHIC ELEMENTS HAVING AN ANCHORING SUBSTRATUM
COMPOSED OF A WATER-INSOLUBLE VINYL PYRIDINE POLYMER
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PHOTOGRAPHIC ELEMENTS HAVING AN
ANCHORING SUBSTRATUM COMPOSED
OF A WATER-INSOLUBLE VINYL PYRI-
DINE POLYMER

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This invention relates to photographic elements, and more particularly, to such elements which have a novel and improved substratum layer for anchoring water-permeable colloid layers to the support.

An object of this invention is to provide new and improved photographic elements. A further object is to provide photographic elements with improved anchoring substratum layers. A related object is to provide photographic film elements with hydrophilic colloid layers which adhere strongly to the support by means of an improved anchoring substratum. Another object is to provide a simple and effective method and means for anchoring water-permeable colloid layers to water-insensitive or hydrophobic supports. 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 present invention. The elements consist of a support having on at least one surface of the support an anchoring substratum composed of a water-insoluble vinylpyridine polymer and a hydrophilic colloid layer on at least one of the said polymer layers. The colloid layers may support still other layers.

The novel elements can be made by coating a support, such as a cellulose derivative, superpolymer, e. g., nylon, polyvinyl chloride, polyethylene, glass, water-proofed paper, etc., with a solution of a water-insoluble vinylpyridine polymer to form a thin layer. A solution, emulsion, or dispersion of a hydrophilic colloid is then coated onto the dried vinylpyridine polymer layer. Additional layers may then be coated on the colloid layers.

It is generally advantageous to use a solvent which is volatile and softens or "bites" the surface of the support for the water-insoluble vinylpyridine coating solution. It is also advantageous to add a small amount of an acid to the aqueous coating solutions used to deposit a hydrophilic colloid or other layer on the vinylpyridine polymer layer. The acid causes the solution to etch or "bite" the surface of the said polymer layer and improves the adherence between the layers.

It has been found that the vinylpyridine polymer layers are clear and have excellent adhesion to hydrophobic materials in general and to hydrophilic colloid silver halide emulsion layers. The vinylpyridine polymer layers do not have any deleterious effect on the light-sensitivity or stability of silver halide emulsion layers which is advantageous.

The vinylpyridine polymers can be made by polymerizing a monomeric vinylpyridine, e. g.,

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alpha-, beta-, or gamma-vinylpyridine or a homologue thereof containing an alkyl radical of one to four carbon atoms in the pyridine ring, in a liquid medium by the aid of a polymerization catalyst. An organic solvent solution can be used if desired in which case inert organic solvents are used. However, emulsion polymerization is quite useful and bulk polymerization methods are effective. The polymerization is preferably carried out in an aqueous mineral acid solution or medium in the presence of a peroxy compound catalyst at temperatures from about 20° to 50° C. for a period of ten or less to 200 or more hours. The proportion of mineral acid, e. g., hydrochloric or sulfuric, may vary over a fairly wide range, e. g., from 0.5 to 2.5 mols of acid per mol of vinylpyridine monomer. The resulting solution may be diluted with water and the solution added to a basic solution, e. g., aqueous sodium hydroxide, and the precipitated resin filtered, washed, and dried. A neutralizing agent can be present in the wash water.

In making the copolymers, there may be used such materials as methyl or ethyl acrylates; methyl, ethyl, isobutyl, and methoxyethyl methacrylates; methacrylamide and N-methylacrylamide; acrylonitrile and methacrylonitrile; styrene; vinyl naphthalene, and the like or mixtures of two or more of these compounds.

In a preferred aspect of the invention, the polymers of unsubstituted alpha or 2-vinylpyridine or its interpolymers containing 1 to 20% of a different interpolymersoluble monomer are used. Such polymers are non-water-soluble, synthetic resins soluble in alcohols, e. g., methyl, ethyl, propyl, and butyl, and mixtures of such alcohols with ketones, e. g., acetone, methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone or in certain chlorinated hydrocarbons, e. g., trichlorethylene.

A practical method of forming the novel anchoring substratum is as follows: The particular vinylpyridine polymer is dissolved in a water-miscible alcohol, preferably methanol or ethanol, in an amount of 0.25% to 20% by weight of the alcohol. The solution is then applied to or coated onto a surface of the support by any of the conventional methods used in making photographic elements. Thus the solutions can be applied from a hopper provided with a doctor blade, dipping, by transfer or beading rollers, or spraying and the solvent removed by allowing it to evaporate, drying, etc.

In the accompanying drawing which constitutes part of this specification:

Fig. 1 is an enlarged section of the film element described in Example I,

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Fig. 2 is an enlarged section of the film element described in Example II,

Fig. 3 is an enlarged section of the film element described in Example IV,

Fig. 4 is an enlarged section of the film element described in Example V,

Fig. 5 is an enlarged section of the film element described in Example VI,

Fig. 6 is an enlarged section of the film element described in Example VII,

Fig. 7 is an enlarged section of the film element described in Example VIII,

Fig. 8 is an enlarged section of the film element described in Example IX,

Fig. 9 is an enlarged section of the film element described in Example X.

The invention will be further illustrated but is not intended to be limited by the following examples. The parts are by weight and the vinylpyridine polymer made by polymerizing unsubstituted 2-vinylpyridine.

EXAMPLE I

A 4% solution of polyvinylpyridine in methanol/ethanol (56/40 by weight) is applied to a cellulose nitrate base 1 and the resulting layer 2 is dried for about two minutes at about 60° C. A 3% solution of a completely hydrolyzed ethylene/vinyl acetate copolymer of the kind described in United States Patent 2,397,866 in ethanol-water (2:7 ratio) containing 1 cc. of glacial acetic acid per 100 cc. of solution is coated onto the polyvinylpyridine layer. A hydrolyzed ethylene/vinyl acetate copolymer silver halide emulsion of the type described in said patent is coated over the clear hydrolyzed ethylene/vinyl acetate layer 3 and resulting emulsion layer 4 is dried at about 60° C. The resulting film element has excellent wet and dry anchorage. The silver halide emulsion layer evidenced no tendency to separate during development in a standard hydroquinone metal developing solution nor during fixing in a 25% sodium thiosulfate bath containing approximately 1% of acetic acid.

EXAMPLE II

A 3% solution of polyvinylpyridine in methanol is applied to a cellulose nitrate base 1 and the resulting layer 2 is dried for about two minutes at about 60° C. A 3% solution of a completely hydrolyzed ethylene/vinyl acetate copolymer in ethanol/water (2:7 ratio) containing 1 cc. of concentrated acetic acid per 110 cc. of said solution is coated onto the polyvinylpyridine layer. A dispersion of colloidal silver in a similar 3% solution of said copolymer free from acid is coated onto the copolymer layer 3. The layers have excellent anchorage to each other and to the support.

A silver halide emulsion layer 4 of the kind described in Example I can be coated onto the colloidal silver layer 5, if desired, and additional emulsion layers coated in like manner.

EXAMPLE III

A 3% solution of polyvinylpyridine in a mixture of acetone and methanol having a ratio of 11 to 2 by volume is coated onto a cellulose acetate film and dried two minutes at 60° C. A solution of a completely hydrolyzed ethylene/vinyl acetate copolymer containing 1 cc. of concentrated acetic acid per 110 cc. of solution is coated onto the polyvinylpyridine layer. A colloidal silver dispersion of the kind described in Example II is coated onto the clear layer of copolymer and

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dried. The layers have excellent wet and dry adherence.

Silver halide emulsion layers can be coated onto the layer of colloidal silver. A layer of polyvinylpyridine can be coated on the other surface of the film in like manner and a light-sensitive silver halide emulsion coated thereon as described in Example I.

EXAMPLE IV

A 3% solution of polyvinylpyridine in a mixture of acetone and methanol having a ratio of 11 to 2 by volume is coated onto a cellulose acetate film 6 and dried two minutes at 60° C. A gelatin solution of the following composition:

	Per cent
Gelatin	2
Acetic acid (glacial)	1
Methanol	87
Water	10

is coated onto the polyvinylpyridine layer 7 and dried for ten minutes at 60° C. A gelatino-silver iodobromide positive type emulsion is coated onto the intermediate gelatin layer 8 and resulting emulsion layer 9 is dried. The superposed layers have good adherence. No evidence of any tendency for the layers to separate is noted after treatment in processing baths.

EXAMPLE V

A 3% solution of polyvinylpyridine in methanol is applied to a cellulose nitrate base 10 and the resulting layer 11 is dried for about two minutes at about 60° C. A 3% solution of a completely hydrolyzed ethylene/vinyl acetate copolymer of the kind described in United States Patent 2,397,866 in ethanol-water (2:7 ratio) containing 1 cc. of glacial acetic acid per 100 cc. of solution is coated onto the polyvinylpyridine layer. A light-sensitive silver halide emulsion is made by precipitating silver halides in an orthosulfobenzaldehyde acetal of polyvinyl alcohol in a manner similar to that described in Example I of United States Patent 2,397,866. The emulsion layer 13 and intermediate layer 12 of hydrolyzed ethylene/vinyl acetate copolymer had excellent adherence to the base by virtue of the anchoring substratum of polyvinylpyridine.

EXAMPLE VI

A polyvinylchloride film base 14 is coated with a thin substratum 15 from a solution of a water-insoluble methyl methacrylate-2-vinylpyridine copolymer in trichlorethylene. An aqueous solution containing 2% of gelatin and 5% of glacial acetic acid by weight is coated onto the copolymer and dried. A gelatino-silver halide emulsion is coated onto the gelatin substratum 16 forming emulsion layer 17. The resulting film exhibits good anchorage between the coated layers.

EXAMPLE VII

A polyvinylchloride film base 18 was coated with a 6% solution of polyvinylpyridine in equal parts of trichlorethylene and methanol. A thin layer 20 of polyvinyl alcohol containing boric acid is coated onto the resulting polyvinylpyridine layer 19 and a silver halide emulsion of the type described in Example I is coated onto the polyvinyl alcohol layer to form emulsion layer 21. The layers had good wet and dry anchorage.

EXAMPLE VIII

A solution of 5-ethyl-2-vinylpyridine polymer

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containing three parts of the polymer in 57 parts of ethanol and 40 parts of acetone is applied to a cellulose nitrate base 22 and the resulting layer 23 is dried for about two minutes at about 60° C. A 3% solution of a completely hydrolyzed ethylene/vinyl acetate copolymer of the kind described in United States Patent 2,397,866 in ethanol-water (50 parts to 47 parts by weight) containing 5 cc. of glacial acetic acid per 100 cc. of solution is coated on the 5-ethyl-2-vinylpyridine polymer layer and dried at about 60° C. A hydrolyzed ethylene/vinyl acetate copolymer silver halide emulsion layer 25 of the type described above is coated over the clear hydrolyzed ethylene/vinyl acetate layer 24 and dried at about 60° C. The resulting film element has satisfactory wet and dry anchorage after processing.

EXAMPLE IX

For the 5-ethyl-2-vinylpyridine polymer solution used in Example VIII is substituted a solution of vinylpyridine/methyl methacrylate copolymer (80/20 by weight) containing three parts of the polymer in 57 parts of ethanol and 40 parts of acetone. The resulting film element has satisfactory wet and dry anchorage after processing. This film element is shown in Fig. 8 of the drawing and consists of cellulose nitrate film base 22 having superposed thereon in order a vinylpyridine/methyl methacrylate copolymer layer 23', hydrolyzed ethylene/vinyl acetate copolymer layer 24 and hydrolyzed ethylene/vinyl acetate copolymer-silver emulsion layer 25.

EXAMPLE X

For the 5-ethyl-2-vinylpyridine polymer solution used in Example VIII is substituted a solution of vinylpyridine/styrene copolymer (80/20 by weight) containing three parts of the polymer in 57 parts of ethanol and 40 parts of acetone. The resulting film element has satisfactory wet and dry anchorage after processing. This film element is shown in Fig. 9 of the drawing and consists of cellulose nitrate film base 22 having superposed thereon in order a vinylpyridine/styrene copolymer layer 23'', hydrolyzed ethylene/vinyl acetate copolymer layer 24 and hydrolyzed ethylene/vinyl acetate copolymer-silver halide emulsion layer 25.

EXAMPLE XI

A 3% solution of poly-2-vinylpyridine in methanol/ethanol (1:1 by weight) is applied to a cellulose nitrate base and the resulting layer is dried for two minutes at about 60° C. A hydrolyzed ethylene/vinyl acetate copolymer silver halide emulsion of the type described in United States Patent 2,397,866 containing 1 cc. of glacial acetic acid per 100 cc. of emulsion is coated over the poly-2-vinylpyridine layer and dried at about 60° C. The resulting film element has good wet and dry anchorage after normal processing.

The hydrolyzed ethylene/vinyl acetate copolymer silver halide emulsion of Examples I to V inclusive and Examples VII to X inclusive was made as follows:

Procedure A

A

240 cc. 0.5N aqueous KI
1680 cc. water

B

1390 cc. 3N AgNO₃
825 cc. 11.6N NH₄OH
1680 cc. water

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C

4800 g. of a 10% aqueous solution of a hydrolyzed interpolymer of ethylene/vinyl acetate containing 5% by weight of ethylene

1465 cc. 3N ammonium bromide
1200 cc. water

A and B at 77° F. were added simultaneously to C at 112° F. over a period of two minutes and 50 seconds. The temperature was then maintained at 112° F. for 15 minutes, the mixture being stirred for the first five minutes of the heat treatment. The resulting mixture was then coagulated with 15% sodium sulfate solution and washed, etc. in the usual manner.

The copolymer silver halide emulsion of Example XI was made as follows:

Procedure B

A

250 cc. 3N AgNO₃
150 cc. 20% NH₄OH
200 cc. water

B

255 cc. 3N NH₄Br
100 cc. water
25 g. hydrolyzed ethylene/vinyl acetate copolymer of procedure A

C

100 cc. glacial acetic acid

D

275 g. hydrolyzed ethylene/vinyl acetate copolymer of procedure A

B is brought to 112° F. and A added at 95° F. in 30 seconds. The mixture is stirred one minute and then C is added at room temperature. The mixture is then cooled to 100° F. and D is added at 120° F. in 30 seconds. The emulsion is then chilled, washed, etc. in a conventional manner.

Various radiation-sensitive materials may be present in the layers coated onto the anchoring substrata. In addition to light-sensitive silver salts, such as silver chloride, silver bromide, silver-chloride-bromide, silver-chloride-iodide and similar mixtures, there may be utilized bichromated hydrophilic colloids, e. g., albumin, gelatin, gum arabic, polyvinyl alcohols, or glue. Immobile color formers, dye intermediates, or dyes may be present in such layers. Other materials include light-sensitive iron salts and diazonium compounds with or without coupling components. With certain of these light-sensitive materials, e. g., the diazo compounds, the binding agent may have a low sensitivity to water. Thus, polyvinyl acetate or a cellulose acetate may be used as the colloidal binder.

The invention is not limited to the use of the specific film bases described in the examples but may be used with practically any transparent film. The polyvinylpyridine layers are adherent to various other film materials, e. g., polyamides, cellulose nitrate, polyvinyl acetals, cellulose propionate, cellulose mixed esters, cellulose ethers, vinyl chloride copolymers, styrene, acrylonitrile copolymers, polyesters, vinyl acetate copolymers, vinyl fluoride copolymers, polyvinyl alcohol, transparentized paper, etc.

These substrata are not necessarily used alone to join the support and light-sensitive layer but may, if desired, be used in conjunction with other substratum layers, such as gelatin, water-sensitive cellulose esters, water-proofing layers, and filter layers. Also, it is possible to incorporate

removable or bleachable silver and antihalation dyes in these layers.

The vinylpyridine polymer layer being an acid acceptor will screen out acidic decomposition products produced by the base material and thus protect the superimposed sensitized layer from the deleterious effects of such acid decomposition products.

The products of this invention have wide application in the general field of photography depending upon the type of water-permeable colloid layers attached to the support. When light-sensitive silver halide dispersions in water-permeable binders are employed, these elements are useful in producing the common photographic negatives and cine positives. The films are also useful in producing matrices for printing or dye transfers and for use in the graphic arts in general. Color films using these substrata are especially useful since the substrata contain no migratory or volatile acidic compounds which can cause fading of the colors. The products also have utility in fields outside of photography, e. g., in special adhesive uses and in the treatment of textiles.

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 laminated photographic element comprising a support, a water-permeable organic colloid layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films, said element having a layer of a light-sensitive silver halide emulsion.

2. A laminated photographic element comprising a water-insensitive film support, a water-permeable colloid layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films, said element having a layer of a light-sensitive silver halide emulsion.

3. A laminated photographic element comprising a support, a water-permeable organic colloid layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble poly-2-vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films, said element having a layer of a light-sensitive silver halide emulsion.

4. A laminated photographic element comprising a water-insensitive film support, a water-permeable colloid layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble poly-2-vinylpyridine polymer which is soluble in methanol and ethanol and mixture of such solvents and forms clear resin films, said element having a layer of a light-sensitive silver halide emulsion.

5. A laminated photographic element comprising a support, a water-permeable colloid silver halide emulsion layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films.

6. A laminated photographic element comprising a water-insensitive film support, a water-permeable colloid silver halide emulsion layer anchored to a surface of the support by means of an intercalated layer composed of a water-insoluble vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films.

7. A photographic element comprising a water-insensitive cellulose derivative film base, a light-sensitive, gelatino silver halide emulsion layer anchored to a surface of the film base by means of an intercalated layer composed of a water-insoluble vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films.

8. A photographic element comprising a water-insensitive cellulose derivative film base, a light-sensitive, gelatino silver halide emulsion layer anchored to a surface of the film base by means of an intercalated layer composed of a water-insoluble poly-2-vinylpyridine polymer which is soluble in methanol and ethanol and mixtures of such solvents and forms clear resin films.

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