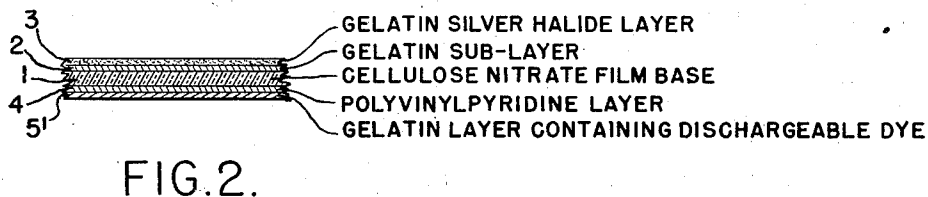
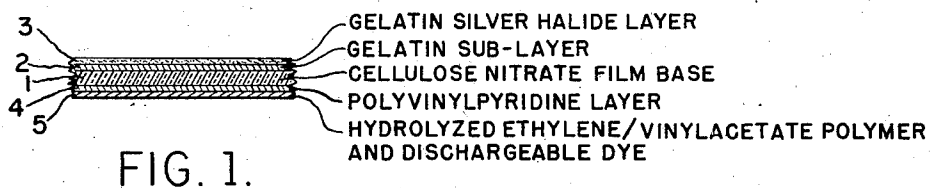


Sept. 7, 1948.

F. P. ALLES
PHOTOGRAPHIC ELEMENTS HAVING A SILVER HALIDE
LAYER AND AN ANTIHALATION LAYER
ON A POLYVINYLPYRIDINE LAYER
Filed April 5, 1947

2,448,508



INVENTOR.

FRANCIS PETER ALLES

BY

Lynn Barratt Morris

ATTORNEY

UNITED STATES PATENT OFFICE

2,448,508

PHOTOGRAPHIC ELEMENTS HAVING A SILVER HALIDE LAYER AND AN ANTIHALATION LAYER ON A POLYVINYLPIRIDINE LAYER

Francis Peter Alles, North Plainfield, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application April 5, 1947, Serial No. 739,645

3 Claims. (Cl. 95—9)

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This invention pertains to photographic elements and to their manufacture. More particularly, it pertains to light-sensitive photographic elements which have light-absorbing colloid layers and anchoring substrata therefor. Still more particularly it pertains to photographic film elements which have antihalation layers and anchoring substrata therefor which are composed of vinylpyridine polymers.

An object of this invention is to provide new photographic elements. Another object is to provide photographic elements with improved antihalation layers. A further object is to provide new means for anchoring antihalation layers to photographic supports. Still other objects will be apparent from the following description of the invention.

The novel photographic elements of this invention consist of a support which is transparent to certain wave lengths of light and has superimposed on one surface thereof a colloid silver halide emulsion layer and on the other surface, in order, a water-insoluble vinylpyridine polymer layer and a water-permeable colloid layer which contains a dischargeable dye that absorbs light of wave lengths to which the emulsion layer is sensitive. The dyes should be dischargeable during photographic processing in the developing and/or fixing bath.

The layer containing the dischargeable dye may be composed of various water-sensitive polymeric materials including water-soluble and hydrophilic polymeric materials, e. g., gelatin, casein, starch, cellulose derivatives including methyl cellulose, ethyl cellulose, cellulose glycollate, low substituted cellulose acetate, polyvinyl alcohols, hydrolyzed ethylene vinyl acetate copolymers and compatible mixtures thereof. The preferred binding agent for the dischargeable dye is composed of the hydrophilic hydrolyzed ethylene/vinyl acetate copolymers described in McQueen United States Patent No. 2,397,866.

The novel elements can be made as follows: A vinylpyridine polymer, e. g., poly-2-vinylpyridine, is dissolved in a water-miscible, volatile alcohol in an amount of 1 to 5% by weight of the alcohol and the resulting solution is coated onto a suitable support, e. g., a transparent film base, and dried. This may be accomplished by any of the conventional coating methods, such as coating from a hopper, immersing, by transfer or beading rollers, spraying, etc., and the solvent is removed by evaporating or drying.

An aqueous solution containing the water-soluble or hydrophilic polymer, the dischargeable

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dye, and a small amount of an acid, e. g., acetic, hydrochloric, sulfuric, etc., is prepared and coated onto the substrata of the vinylpyridine copolymer and then dried. A light-sensitive layer, such as a colloid silver halide emulsion layer, is then coated onto the opposite side of the base.

The acid causes a superficial softening of the surface of the vinylpyridine polymer layer and this causes the antihalation layer to fastly adhere to the substrata. It is not necessary to add the acid to the coating solution for the antihalation layer as the surface of the vinylpyridine polymer layer can be wetted with a dilute aqueous solution of an acid and an aqueous solution containing the water-sensitive polymer and the dischargeable dye is coated onto the acid-treated surface of the vinylpyridine copolymer layer.

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

The invention is not limited to the use of polyvinylpyridines, including the alkyl substituted polyvinylpyridines, for the anchoring substratum as copolymers soluble in 1% aqueous acetic acid which contain up to 20% of another polymerizable vinyl or vinylidene compound having a single vinyl group ($\text{CH}_2=\text{C}<$) are useful. Suitable compounds for copolymerization with a monomeric vinylpyridine are styrene, acrylic esters and amides, alpha-alkyl-substituted acrylic esters and amides, acrylonitriles and methacrylonitriles.

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; sty-

In a preferred aspect of the invention, the polymers of unsubstituted alpha or 2-vinylpyridine or its interpolymers containing 1 to 10% of a different interpolymers 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. They form clear, light-colored, nontacky films or coatings which are readily and completely soluble in dilute aqueous acids, e. g., acetic, hydrochloric, sulfamic, sulfuric, phosphoric, and oxalic acids.

There are many commercially available dischargeable dyes which can be used in the anti-halation layers. Among such classes of dyes are the fuchsone dyes which contain one or more carboxyl groups, e. g., aurin dicarboxylic acid and hydroxycarboxy-fuchsone, etc., which are described in German Patent 512,613 and United States Patent 1,879,537; the mono- and polycarboxylic acids of aminotriphenyl dyes of German Patent 541,596, e. g., fuchsin mono-, di-, and tri-carboxylic acids and aniline blue di- and tri-carboxylic acids; the triphenylmethane dyestuffs with two hydroxyl groups of German Patent 541,118, e. g., benzaurin and tetrabrombenzaurin; the styryl dyes of German Patent 518,363 derived from quinalin-alkyl halides or benzothiazole alkyl halides with paradialkylbenzaldehydes. These dyes are discharged readily in alkaline photographic developers and are not restored to color by fixing. Still other useful dyes are described in United States Patent 2,036,546 and British Patent 8956 of April 28, 1894.

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

A transparent cellulose nitrate film base is coated with a 3% by weight solution of polyvinylpyridine in a methanol-ethanol mixture (60/40 by weight) and the resulting layer 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

Methyl-p-aminophenol hydrosul-	
fate -----	grams-- 5.0
Hydroquinone -----	do----- 7.5
Sodium sulfite -----	do----- 60.0
Sodium carbonate -----	do----- 58.5
Potassium bromide -----	do----- 4.5
Water to make -----	cc----- 1000.0

The film element described in this example is illustrated in Fig. 1 of the drawing wherein the cellulose nitrate film base 1 has on one surface a gelatin sublayer 2 on which there is coated gelatin silver halide sublayer 3. The reverse surface of the base is coated with a thin layer 4 composed of polyvinylpyridine on which is deposited a hydrolyzed ethylene/vinylacetate copolymer layer 5 containing a dischargeable dye.

A transparent cellulose nitrate film base is provided with a thin layer of polyvinyl pyridine as described in Example I. A 3% aqueous solution of gelatin containing 1% of acetic acid and 1% of acid magenta (Color Index No. 692) dye is coated onto the polyvinylpyridine layer and dried. A thin gelatin substratum is coated onto the reverse side of the film base onto which is coated a panchromatic gelatino-silver iodobromide emulsion layer. The antihalation layer has excellent adherence to the polyvinyl pyridine layer which in turn has excellent adherence to the film base. The film is exposed and processed after the manner described in Example I with similar results.

The film element described in this example is illustrated in Fig. 2 of the drawing wherein the cellulose nitrate film base **1** has on one surface a gelatin sublayer **2** on which there is coated gelatin silver halide sublayer **3**. The reverse surface of the base is coated with a thin layer **4** composed of polyvinylpyridine on which is deposited a gelatin layer **5'** containing a dischargeable dye.

In place of the specific dischargeable dyes of the foregoing examples, there can be substituted various other dyes including Pontamine Fast Red F (Color Index 419), absorption very strong below 5600 Å, Du Pont Purpurine 10B (Color Index 495), absorption very strong below 5600 Å, Pontamine Scarlet B (Color Index 382), absorption below 5400 Å, Congo Red (Color Index 370), good absorption 3900-5600 Å, Pontamine Blue RW (Color Index 512), strong absorption above 5600 Å, Niagara Blue R (Color Index 515), strong absorption 5150-6000 Å, National Fast Green B (Color Index 667), Victoria Green (Color Index 657), Red Violet 5RS (Color Index 693), Pontacyl Green B (Color Index 666), Fuchsin (Color Index 677). The Color Index numbers referred to above are those of the Colour Index of The Society of

Dyers and Colourists, edited by F. M. Rowe D. Sc., F. I. C., First Edition, published by the Society at 30 Pearl Assurance Buildings, Bradford, Yorkshire, England.

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.

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.

An advantage of the invention is that it provides photographic elements with light-absorptive or anti-halation layers which have excellent dry anchorage to a film base by means of the vinylpyridine polymer layer. The layers thus formed are more resistant to abrasion and flexing than comparable gelatin layers. They do not become tacky under conditions of high humidity and temperature as does gelatin.

What is claimed is:

1. A photographic element comprising a support which transmits light rays, a light-sensitive silver halide emulsion layer on one side of the support, a sublayer on the opposite side of the support consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid which carries a water-permeable colloid layer containing a dischargeable dye which absorbs light of wave lengths to which the emulsion is sensitive.

2. A photographic element comprising a transparent film support, a light-sensitive silver halide emulsion layer on one side of the support, a sublayer on the opposite side of the support consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid which carries a water-permeable colloid layer containing a dischargeable dye which absorbs light of wave lengths to which the emulsion is sensitive.

3. A photographic element comprising a transparent film support, a light-sensitive silver halide emulsion layer on one side of the support, a sublayer on the opposite side of the support consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid which carries a hydrophilic hydrolyzed ethylene/vinyl acetate copolymer containing a dischargeable dye which absorbs light of wave lengths to which the emulsion is sensitive.

FRANCIS PETER ALLES.

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