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PHOTOGRAPHIC ELEMENTS HAVING ANTIHALATION LAYERS COMPOSED OF VINYLPYRIDINE POLYMERS AND ANTIHALATION MATERIALS

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PHOTOGRAPHIC ELEMENTS HAVING ANTIHALATION LAYERS COMPOSED OF VINYLPYRIDINE POLYMERS AND ANTIHALATION MATERIALS

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8 Claims. (Cl. 95—9)

1

This invention relates to photographic elements and, more particularly, to photographic film elements bearing a novel, removable, antihalation layer on the reverse side. Still more particularly it relates to photographic film elements having an antihalation layer wherein the binding agent is composed of a vinylpyridine polymer.

An object of this invenion is to provide new and useful film elements which have removable antihalation layers. Another object is to provide such elements wherein the layers do not come off during alkaline development of the exposed element. A further object is to provide such elements wherein the antihalation layer can be readily removed after development in a weak acid-containing bath. A still further object is to provide such elements which are free from stain after removal of the antihalation coating. Another object is to provide antihalation layers which do not deleteriously affect the sensitivity of silver halide emulsion layers. Yet another object is to provide antihalation layers which do not deteriorate, become insoluble, or become tacky on storage. Still other objects will be apparent from the following description of the invention.

It has been discovered that the vinylpyridine polymers are eminently well suited as the film-forming binding agent for the antihalation layer of a photographic element disposed on the reverse side of a photographic film. The layers are not dissolved by the alkaline developer or water rinse baths used after development. However, they are solubilized by the acid present in and at the concentration usually employed in the ordinary acid photographic processing baths, such as acid stop baths, acid fixing baths, acid hardening fixing baths, acid bleach baths, reversal bleach baths, etc. They are removable in acid developing baths.

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 proportion of mineral acid, e. g., hydrochloric

2

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.

The invention is not limited to the use of polyvinylpyridine, including the alkyl substituted polyvinylpyridines, as the binding agents for the antihalation materials because copolymers soluble in 1% aqueous acetic acid which contain up to 20% of another polymerizable vinyl or vinylidene compound having a single vinyl group ($CH_2=C<$) 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; 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 10% of a different interpolymerizable 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, non-tacky films or coatings which are readily and completely soluble in dilute aqueous acids, e. g., acetic, hydrochloric, sulfamic, sulfuric, phosphoric, and oxalic acids.

A practical method of forming the antihalation layer is as follows: The vinylpyridine polymer is dissolved in a water-miscible alcohol in an amount of 0.25 to 20% by weight of the alcohol and an antihalation material admixed therewith. Thus antihalation pigments or dyes may be added in the form of small particles and dispersed or milled into the solution. Water-tolerant or spirit-soluble dyes can be added from a solvent solution. The solution is then applied to or coated on the back of a film base by any of the conventional coating methods, e. g., coating from a hopper provided with a doctor blade, dipping, by

transfer or beading rollers, spraying, etc., and the solvent allowed to evaporate. A layer in the order of 1 to 10 microns is generally sufficient. However, substantially thicker layers can be made if desired. A light-sensitive layer, e. g., a colloid silver halide emulsion layer, is then coated on the opposite side of the base.

The nature of light-absorption characteristics of the antihalation material for the layer will, of course, depend upon the particular characteristics of the emulsion. They are added in sufficient amounts to form an effective density which will stop the passage of the undesired light rays. Halation of blue-sensitive and ortho-chromatic emulsions can be minimized by the use of black and red non-halation layers. Panchromatic emulsions, theoretically, require black non-halation layers, although green and deep blue can be used advantageously. Natural occurring pigments of the above-mentioned colors may be used by this invention since the entire non-halation coating is removed during processing. Metallo-dye complexes and inorganic, colored compounds are likewise suitable if they are of appropriate colors and have no adverse effect on the photographic emulsion which comes into contact with the non-halation layer when rolled up.

In assignee's copending application of Francis Peter Alles, Serial No. 687,709, filed August 1, 1946, there are disclosed and claimed related antihalation photographic elements which consist of a transparent support which have a light sensitive silver halide emulsion on one side and on the other side, in order, a thin, clear vinylpyridine polymer layer; next, an antihalation layer composed of a vinylpyridine polymer having dispersed therethrough an antihalation dye or pigment; and, finally, an antiabrasion layer. The vinylpyridine polymers of subject application have the same characteristics as the vinylpyridine polymers described in the present application.

The invention is illustrated in the accompanying drawing, the single figure of which is a cross-section of the element, showing the transparent film support 1, colloid silver halide emulsion layer 2 and antihalation layer 3 of vinylpyridine polymer and antihalation material.

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

Example I

A coating solution having the following composition:

Milori Blue	grams	4.0
Polyvinylpyridine	do	6.0
Methanol	cc	50.0

was prepared by grinding the ingredients in a ball mill for 20 hours. The resulting mixture was diluted to 200 grams total weight by the addition of methanol and then coated onto the back side of a transparent cellulose acetate film base and allowed to dry. The front side of said film base was coated with a gelatino-silver halide panchromatic emulsion. The antihalation layer was smooth, strongly adherent, uniform, free from tackiness, and was not affected by the development of the exposed element in an alkaline metol-hydroquinone developer. Nor did it contaminate the developer. The antihalation coating was readily removed with a 1% acetic acid bath and washed with water. No stain or pigment particles remained on the back of said film.

Example II

Milori Blue	grams	3.0
Polyvinylpyridine	do	6.0
Lecithin	do	1.2
Methanol	cc	50.0

were treated as in Example I except that the grinding period was extended to three days.

Example III

Cellulose acetate film base was coated with a 3% solution of polyvinylpyridine in methanol and then coated with a 1% solution of Victoria Blue BX in methanol. The coating and removal characteristics were similar to Example I. Similar results were obtained with 1% Ink Blue and 1% Rotalin Blue.

Example IV

Cellulose acetate film base was coated with a solution of 1% polyvinylpyridine in methanol. After drying, it was over-coated on the treated side with a 3% polyvinylpyridine solution containing 1% Luxol Fast Black L (1944 yearbook of the American Association of Textile Chemists and Colorists, vol. XXI, page 336). The coating and removal characteristics were similar to those described in Example III.

Example V

A composition was prepared as in Example I using:

	Per cent
Ink blue	0.4
Polyvinylpyridine	3.0
Acid Magenta O	0.4

in 80% aqueous methanol. A cellulose acetate film base was coated and processed as in Example I with similar results.

Example VI

A stock solution was prepared consisting of:

Milori Blue	grams	2.0
Sulfanthrene Pink FFS	do	2.0
Polyvinylpyridine	do	9.0
Methanol	cc	60.0

Said solution was divided into three equal parts. Each part was diluted to 100 cc. with methanol and 0.2 gram, 0.4 gram, and 0.6 gram of Lecithin added to the samples respectively. When coated in the manner described in Example I, the coating containing the 0.4 gram of Lecithin was slightly superior, but all gave excellent non-halation coatings completely removable from the film bearing a gelatin silver halide panchromatic emulsion layer on the front side in 1% acetic acid followed by a water rinse.

If it is desired to remove the antihalation layer before fixation, it may be solubilized by immersing the film in weak acid baths, e. g., acetic or citric acid baths, which are commonly employed as a stop bath between the development and fixation stages of processing.

In general, any dye or pigment which possesses the property of absorbing actinic light, of being readily dissolved or destroyed in ordinary photographic baths and of not injuring such baths may be used. The dye or dyes to be used in any specific instance are primarily determined by the light-sensitivity of the emulsion. Such emulsions are usually gelatin silver halide emulsions which contain sensitizers, such as cyanine, carbocyanine, pseudo-cyanine, cyazine bases, and salts. That is, it must be absorptive of light of the wave-

lengths to which the emulsion is sensitive. In general, the dye should be added in an amount sufficient to give a photographic density of 0.2 to 0.8 or the amount of dyed layer should be sufficient to give such a density. When added from ethanol, etc., a very fine subdivision of the dye in the layer is obtained. As examples of additional useful dyes, mention is made of:

Auramine (C. I. 655)
Helianthin (C. I. 142, 146)
Brilliant Yellow S (C. I. 144)
Chrysoin (C. I. 148)
Acid Blue Black (C. I. 246)
Rhodamine (C. I. 749, 750, 751, 746, 753, 761, 763)
Fuchsin (C. I. 677)
Sufranine G (C. I. 841)
Ponceau 6R (C. I. 186)
Crocein Scarlet (C. I. 277, 251, 286, 252, 291, 183)
Azorubin (C. I. 179)
Sufranine O (C. I. 841)
Ponceau 2R (C. I. 79)
Spirit Solution Nigrosine (C. I. 864)
Metanil Yellow (C. I. 138)

The color index numbers (C. I.) referred to above are identified as follows: "Society of Dyers and Colourists; Colour-Index, F. M. Rowe D. Sc., F. I. C.; First edition January 1924; published by The Society at the General Offices, 30 Pearl Assurance Buildings, Bradford, Yorkshire."

The invention is not limited to the use of cellulose ester film bases 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 and copolymers, styrene, acrylonitrile and copolymers, polyesters, vinyl acetate and copolymers, vinyl fluoride and copolymers, polyvinyl alcohol, transparentized paper, etc.

This invention has the advantage that a nontacky antihalation layer which is insoluble in water or alkaline solutions but is readily soluble in dilute acid baths may be quickly prepared. A further advantage is the fact that stable, nontacky, non-reactive, antihalation layers may be easily prepared. Thus films may be tightly rolled up with the antihalation layer in direct contact with the emulsion layer and stored for long periods of time without any detrimental effects.

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

What is claimed is:

1. A photographic element comprising a support which transmits light, a light-sensitive layer on one side of said support and an antihalation layer on the other side of the support comprising a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid and an antihalation material.

2. A photographic element comprising a film base which transmits actinic light, a light-sensitive colloid-silver halide emulsion layer on one surface of said film base and an antihalation layer on the other surface of the film base consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid, said polymer layer having dispersed therethrough an antihalation material, said support transmitting light of wavelengths to which the emulsion layer is sensitive.

3. A photographic element comprising a film base which transmits actinic light, a light-sensitive colloid-silver halide emulsion layer on one surface of said film base and an antihalation layer on the other surface of the film base consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid, said polymer layer having uniformly dispersed therethrough finely divided particles of an antihalation material which is absorptive of the rays to which the silver halide emulsion layer is sensitive.

4. A photographic element comprising a transparent cellulose ester film base, a light-sensitive colloid-silver halide emulsion layer on one surface of said film base and an antihalation layer on the other surface of the film base consisting of a water-insoluble vinylpyridine polymer which is soluble in 1% aqueous acetic acid, said polymer layer having uniformly dispersed therethrough finely divided particles of an antihalation material which is absorptive of the rays to which the silver halide emulsion layer is sensitive.

5. A film element of the type set forth in claim 4 wherein the emulsion layer is a panchromatic emulsion layer.

6. A film element of the type set forth in claim 4 wherein the emulsion layer is a panchromatic emulsion layer and the antihalation material absorbs actinic light which exposes such a layer.

7. A photographic element comprising a transparent film base, a light-sensitive colloid-silver halide emulsion layer on one surface of said film base and an antihalation layer on the other surface of the film base consisting of a water-insoluble polyvinylpyridine which is soluble in 1% aqueous acetic acid, said polymer layer having uniformly dispersed therethrough finely divided particles of an antihalation material.

8. A photographic element comprising a transparent film base, a light-sensitive colloid-silver halide emulsion layer on one surface of said film base and an antihalation layer on the other surface of the film base consisting of a water-insoluble unsubstituted 2-vinylpyridine polymer which is soluble in 1% aqueous acetic acid, said polymer layer having uniformly dispersed therethrough finely divided particles of an antihalation material.

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