Aug. 12, 1952 W. R. SANER 2,606,834

PHOTOGRAPHIC ELEMENTS WITH LIGHT-FILTERING LAYERS

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FIG. 1.

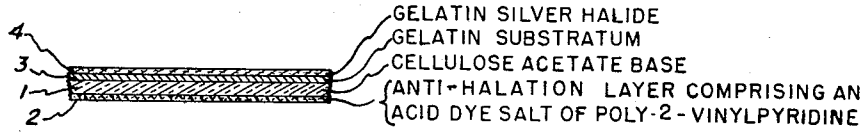


FIG. 2.

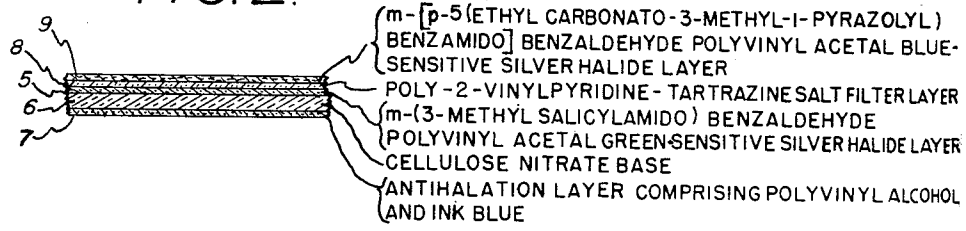
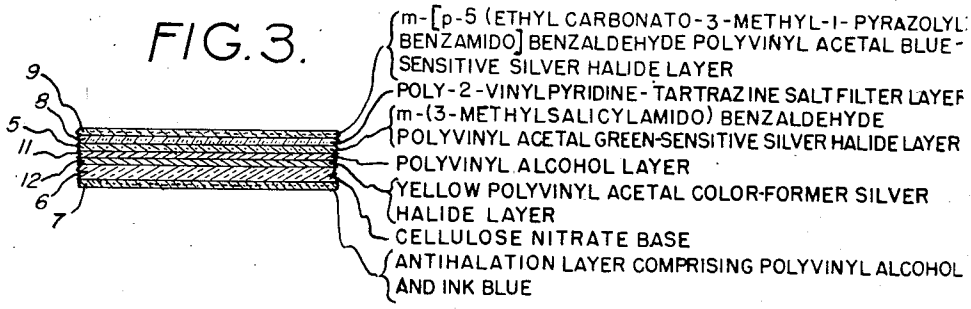


FIG. 3.



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PHOTOGRAPHIC ELEMENTS WITH LIGHT-FILTERING LAYERS

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9 Claims. (Cl. 95—9)

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This invention relates to photography and more particularly to photographic elements such as film, papers, and printing plates which contain a light-filtering layer composed of a salt of a polyvinylpyridine with an acid dye. Still more particularly it relates to photographic film elements which contain a layer composed of a salt of a polyvinylpyridine with a dye containing a carboxylic or sulfonic acid group.

An object of this invention is to provide improvements in the art of photography. Another object is to provide new and useful photographic films, papers, and plates. Another object is to provide photographic film elements with a novel light-filtering layer composed of a salt of a polyvinylpyridine with a dye containing a sulfonic or carboxylic acid group or a mixture of such salts. A still further object is to provide photographic film elements with an anti-halation layer composed of a salt of polyvinylpyridine with a dye containing a sulfonic or carboxylic acid group. Still other objects will be apparent from the following description of the invention.

It has been discovered that water-insoluble vinylpyridine polymers which are soluble in 1% acetic acid form polymeric salts with acid dyes of high molecular weight which contain sulfonic acid or carboxylic acid groups and the resulting salts form practical light-absorbing layers in photographic films and plates. These polymeric salts form hard, smooth layers which are resin-like in appearance but are colored in accordance with the tinctorial properties of the dyes used to form the salts.

The salts of vinylpyridine polymers with the acid dyes may be prepared by admixing in an aqueous medium a vinylpyridine polymer with an acid dye containing a sulfonic acid or carboxylic acid group or groups or a mixture of acid dyes. The polymeric polyvinylpyridine salts precipitate out and can be purified by washing in water and recrystallizing from an organic solvent, e. g., methanol, ethanol, etc. The acid dyes used to form the salts confer a color upon the resulting polymeric salt substantially the same as that of the original dye. The polymeric dye salt or mixture of such salts can be dissolved in a solvent such as methanol or ethanol or a mixture of such solvents, and then coated onto a support or onto a light-sensitive silver halide layer on a support to form a light-filtering layer. A light-sensitive

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silver halide layer may then be coated on the polymeric dye salt layer. Removable anti-halation layers can be made by depositing the polyvinylpyridine salt with the acid dye on one side of a transparent base, e. g., a film or transparentized paper, and a colloid silver halide emulsion layer, or a plurality of such layers which are differentially sensitized may be deposited on the other side of the base. The layer may be readily removed in a dilute acid bath which may be an acid stop-bath or an acid fixing bath after development.

Novel light-filtering layers may be made by depositing the polymeric salt of a polyvinylpyridine with an acid dye onto a colloid silver halide emulsion layer which is disposed on a suitable film base or on another colloid silver halide emulsion layer which is disposed on such a base. A photographic silver halide emulsion layer is then coated onto the novel light-filtering layer. The respective silver halide emulsions are generally differentially sensitized so that they record light from different primary color regions of the spectrum. Thus, a yellow dye salt can be used in a light-filtering layer where it is desired to absorb or prevent blue light from exposing a lower gelatino silver halide emulsion layer which is also sensitive to green or red light. In the case of a multi-layer film containing three differentially sensitized silver halide emulsion layers, a layer composed of a yellow dye salt of a polyvinylpyridine is placed between the outer blue sensitive layer and the next green-blind red sensitive silver halide emulsion layer. A layer composed of a red dye salt of a polyvinylpyridine is placed between the latter layer and the bottom layer which is a green sensitive silver halide emulsion layer. These layers of course are cast from solution in making the multilayer film element.

Any dye salt which possesses the property of absorbing actinic light which will expose the silver halide emulsion layers of the elements can be used for making the anti-halation layers. The dye must be absorptive of light of wave lengths to which the emulsion is sensitized. In some cases, mixtures of two or more different dye salts of the polyvinylpyridines may be used in order to acquire adequate light-absorption. In the case of daylight-loading backings the layers are usually black and absorb all wavelengths of visible light.

Polyvinylpyridines or vinylpyridine polymers

can be made by polymerizing a monomeric vinylpyridine of relatively low molecular weight, e. g., alpha-, beta- or gamma-vinylpyridine, or a homologue thereof containing an alkyl radical of 1 to 4 carbon atoms in the pyridine ring, in a liquid medium by the aid of a vinyl compound polymerization catalyst. An organic solvent solution can be used as the liquid medium, if desired. However, the organic solvent should be inert so that it will not interfere with the polymerization reaction. The polymers can be made by emulsion polymerization, if desired, and bulk polymerization methods are effective. The polymerization is preferably carried out in an aqueous acid solution or medium in the presence of a peroxy compound catalyst at temperatures from about 20 to 50° C. for a period of 10 or less to 200 or more hours. The proportion of mineral acid, e. g., hydrochloric or sulfonic acid, used may vary over a fairly wide range, e. g., from 0.5 to 2.5 moles of acid per mole of vinylpyridine monomer.

The resulting solution may be diluted with water and admixed with a basic solution, e. g., aqueous sodium hydroxide, whereupon a vinylpyridine polymer precipitates and can be washed and dried. In some cases, it is desirable to incorporate a neutralizing agent in the washing solutions to remove any remaining acid catalyst.

The vinylpyridine polymers described above, including the lower alkyl substituted polyvinylpyridines, are of relatively high molecular weight and generally are mixtures of polymeric molecules of various chain lengths. The polymers are soluble in 1% aqueous acetic acid and in similar aqueous solutions of other acids, e. g., hydrochloric, sulfuric, sulphamic, and oxalic and form hard clear resinous films.

The polymers in question need not consist wholly of a single polymerized monomer. On the contrary, a mixture of two or more of the monomeric vinylpyridines described above can be used. In addition, copolymers which contain up to 20% of another polymerizable vinyl or vinylidene compound ($CH_2=C<$) are useful. These compounds may be admixed with the monomeric vinylpyridine, and the polymerization carried out in a similar manner. The copolymers should likewise be soluble in 1% aqueous acetic acid. Suitable compounds for copolymerization are styrene, acrylic esters and amides, alpha-alkyl substituted acrylic esters and amides, and acrylonitrile and methacrylonitrile. Among the specific useful compounds of this type are methyl and ethyl acrylates; methacrylamide and N-methylacrylamide; acrylonitrile and methacrylonitrile. Mixtures of two or more of the latter compounds can be used, if desired.

The proportion of the acid dye which is used to make the polymeric acid dye salt of the polyvinylpyridine may vary over fairly wide limits, e. g., from 0.01 to 0.5 mol of dye per mol of vinylpyridine monomer or vinylpyridine. In general, however, amounts of dye salt from 0.05 to 0.10 mol per mol of vinylpyridine will be sufficient and constitutes a preferred range.

In the case of dyes which have their carboxylic or sulfonic acid group or groups neutralized by a water-soluble salt-forming cation, e. g., alkali metal, ammonium, or amine, the salt-forming reaction with the vinylpyridine polymers must be carried out under acid conditions so that these salts are converted into the free acids. Various organic and inorganic acids may be used. Suitable acids include hydrochloric, sulfuric, and acetic. The acid concentration should be rather low, and sufficient to give a pH in the range of 2 to 3.

It is not necessary to coat the anti-halation layer composed of the polyvinylpyridine acid dye salt directly on the transparent or light-transmitting support. On the contrary, a water-soluble or dilute acid soluble colloid material may be first deposited on the base and the vinylpyridine dye salt deposited thereon. Among the water-soluble colloid materials which can be used are polyvinyl alcohol, hydrolyzed ethylene/vinyl acetate copolymers, gelatin, cellulose ethers, e. g., water-soluble methyl cellulose, cellulose acetate phthalate alkali metal salts. As dilute acid soluble colloids there may be mentioned the polyvinyl pyridines described in U. S. Patent 2,448,525 and deacetylated chitin.

In the preferred aspect of the invention, the polymers of the unsubstituted alpha- or 2-vinylpyridine are used to react with the acid dyes. Poly-2-pyridine is a water-insoluble synthetic resin which is soluble in alcohols, e. g., methyl, ethyl, propyl, and butyl alcohols, and mixtures of such alcohols and also mixtures of these alcohols with ketones, e. g., acetone, methyl ethyl ketone, methyl propyl ketone, and methyl isobutyl ketone. They are also soluble in certain chlorinated hydrocarbons, e. g., trichlorethane and methylene chloride. The polymers form clear, light-colored, non-tacky films or coatings which are readily and completely soluble in dilute aqueous acids, e. g., 1% acetic acid, hydrochloric, sulfamic, sulfuric, phosphoric, and oxalic acids.

The invention will be further illustrated but is not intended to be limited by the following examples:

Example I

0.4 gram of Pontacyl Fast Black BBO (Colour Index 307) in aqueous solution was added to 20 milliliters of a 10% solution of poly-2-vinylpyridine (which was soluble in 1% aqueous acetic acid and formed a clear hard resin-like film), in methanol, whereby a polymeric salt of the acid dye with the poly-2-vinylpyridine was precipitated. The polymeric salt or complex which was isolated was soluble in methanol and ethanol and showed no tendency to bleed in water. A 10% solution of the acid dye salt of poly-2-vinylpyridine in methanol was applied to one surface of a clear cellulose acetate film base **1** as shown in Fig. 1 of the accompanying drawing which constitutes a part of this specification and dried forming a continuous, hard, clear resinous layer **2** of a bluish-green color. The other side of the film base was provided with a thin gelatin anchoring substratum **3**. A gelatin silver chlorobromide emulsion was then coated onto the gelatin substratum and the resulting emulsion layer **4** was dried. The polyvinylpyridine acid dye salt layer had a density of 0.75 as determined by an ERPI densitometer. Its density was found to be sufficient to permit the film to be used in a daylight loading camera spool.

A portion of the film was given a flash exposure and developed for 3 minutes in a developing solution made up by admixing the following components in the order named:

Water	cc.	975.0
p-N-methylaminophenol sulfate	grams	1.4
Sodium sulfite, anhydrous	do	60.0
Hydroquinone	do	6.2
Sodium carbonate, monohydrate	do	56.0
Potassium bromide	do	1.8
Water to make 1.0 liter		

The film was then immersed in a 2% acetic acid bath for a period of one minute. The polyvinylpyridine-acid dye salt layer swelled in the acid bath and was readily washed off the film with slight rubbing, leaving no residual stain. The film was then immersed in a conventional sodium thiosulfate fixing bath for five minutes, washed in running water for 30 minutes and dried. The anti-halation coating or layer 2 of the poly-2-vinyl acid dye salt had no deleterious effect on the emulsion or developing or fixing solutions.

Example II

Another poly-2-vinylpyridine acid dye salt was made in a manner similar to that described in Example I but substituting an equivalent of Pontamine Green BX (Colour Index 593) for the dye described in the preceding example. A photographic film element was prepared in a similar manner and exposed, developed, and further treated as described in the example with similar results. The polyvinylpyridine acid dye salt layer had a density of 0.80 as determined by an ERPI densitometer.

Example III

Another poly-2-vinylpyridine-acid dye salt was prepared in the same manner described in Example I but substituting Pontamine Green S (Colour Index 583) for the dye of Example I. A photographic film element was prepared from this die in a similar manner and exposed, developed, and further treated after the manner described in Example I with similar results. The polyvinylpyridine acid dye salt layer had a density of 0.75 as determined by an ERPI densitometer.

Example IV

A solution of 2.4 grams of the yellow dyestuff Tartrazine (Colour Index 640), in 300 milliliters of water was added to 120 milliliters of a 10% solution of poly-2-vinylpyridine (which polymer was soluble in 1% aqueous acetic acid and formed a clear, hard, resin-like film), in methanol containing 12 milliliters of glacial acetic acid. 150 milliliters of a 2% aqueous solution of ammonium hydroxide were added to the poly-2-vinylpyridine-dye solution, whereby a salt of the acid dye with poly-2-vinylpyridine was precipitated from solution, said salt being washed freely with cold water to remove excess dye. The salt was soluble in a 50/50 mixture of methanol and ethanol. When applied to a clear surface from such a solution, a transparent, hard, resin-like yellow film was obtained.

Seven grams of the above salt were dissolved with stirring in 365 milliliters of 95% ethyl alcohol and 255 milliliters of distilled water at 140–150° F. To this was added a solution composed of 195 milliliters of distilled water, 28 milliliters of 95% ethyl alcohol and 24 grams of polyvinyl alcohol (completely hydrolyzed polyvinyl acetate, 4% aqueous solution having a viscosity at 20° C. of 25 centipoises). Eight milliliters of a 10% aqueous solution of n-cetyl betaine was then added and the total solution stirred at 130° F. for 10 minutes.

A green sensitive cyan polymer emulsion, containing approximately 4% of a m-(3-methyl salicylamido) benzaldehyde polyvinyl acetal of the type described in Martin U. S. application Ser. No. 29,921 filed May 28, 1948 now Patent No. 2,538,257, and 2.1% silver halide, was coated to form green-light-sensitive layer 5 on cellulose nitrate film base 6 as shown in Fig. 2 of the drawing which had previously been treated on the reverse side with a solution of polyvinyl alcohol (77% hydrolyzed polyvinyl acetate, having a viscosity of 20–30 centipoises at 20° C.) containing dissolved therein a quantity of the acid dye known as Ink Blue (Colour Index No. 706). This layer 7 is intended to act as a "non-halation" layer and is dischargeable during processing. Over the cyan layer the dispersion of the polyvinylpyridine-Tartrazine salt described above was applied to form filter layer 8. Finally, a blue sensitive magenta polymer emulsion containing approximately 3% m - [p - 5(ethyl carbonato - 3-methyl - 1 - pyrazolyl) benzamido] benzaldehyde polyvinyl acetal and 1.6% of silver halide, was applied over the polyvinylpyridine-Tartrazine salt layer to form blue-light-sensitive layer 9.

In the film prepared in this manner, the polyvinylpyridine-Tartrazine salt layer acted as a filter layer to blue light, thus reducing "print through" in the green sensitive cyan layer. The tendency of the Tartrazine dye molecules to migrate during coating was also greatly reduced.

The coated films after exposure were developed for 10 minutes in the following color developer:

p-Aminodiethylaniline .HCl	grams	2.5
Sodium sulfite (anhydrous)	do	10.0
Sodium carbonate (monohydrate)	do	29.25
Potassium bromide	do	2.0
Water to make 1.0 liter		

The films were then washed for one minute and "fixed" for five minutes in the following solution:

Sodium thiosulfate (crystals)	grams	240.0
Sodium sulfite (anhydrous)	do	15.0
Borax	do	18.0
Glacial acetic acid	cc	12.0
Potassium alum	grams	20.0
Water to make 1.0 liter		
(Dilute 1 part to 2 of water before using)		

After washing for 10 minutes, the films were bleached in the following solution for five minutes:

Potassium ferricyanide	grams	100.0
Boric acid	do	10.0
Borax	do	5.0
Water to make 1.0 liter		

Films were then washed two minutes and "fixed" again, for five minutes in the following solution:

Sodium thiosulfate crystals	grams	200.0
Water to make 1.0 liter		

After washing for 10 minutes, the films were dried.

The yellow dye was removed during processing.

A similar film element as shown in Fig. 3 of the drawing containing an additional color-forming layer can be made by first coating onto the film base a layer 10 composed of one of the yellow color-forming polyvinyl acetals of McQueen U. S. application Ser. No. 9,330 filed February 18, 1948, now Patent No. 2,513,190, a layer 11 of a medium viscosity polyvinyl alcohol from a 2% solution in 20 to 25% aqueous ethanol is coated onto the polyvinyl acetal layer. Upon the latter layer there are then coated the layers described above. It is processed in like manner with similar results.

Example V

A solution of 2.4 grams of the yellow acid dye described in Example 2 of United States Patent

2,274,782 in 300 milliliters of water was added to 120 milliliters of a 10% solution of poly-2-vinylpyridine (which polymer was soluble in 1% aqueous acetic acid and formed a clear, hard, resin-like film), in methanol containing 12 milliliters of glacial acetic acid. 150 milliliters of a 2% aqueous solution of ammonium hydroxide were added to the poly-2-vinylpyridine-dye solution, whereby a salt of the acid dye with poly-2-vinylpyridine was precipitated from solution, said salt being washed freely with cold water to remove excess dye. The salt was soluble in a 50/50 mixture of methanol and ethanol. When applied to a clear surface from such a solution, a transparent, hard, resin-like film was obtained.

Seven grams of this polyvinylpyridine-dye salt were dissolved with stirring in 370 milliliters of 75% ethyl alcohol and 260 milliliters of distilled water at 140 to 150° F. To this was added a solution composed of 24 grams of polyvinyl alcohol (completely hydrolyzed polyvinylacetate, 4% aqueous solution having a viscosity at 20° C. of 25 centipoises). Eight milliliters of a 10% aqueous solution of n-cetyl betaine were then added, and the total solution stirred at 130° F. for 10 minutes.

A multilayer film was then prepared substituting the above solution for that containing the polyvinylpyridine-dye salt of Example IV.

Processing was carried out as in Example IV with similar results.

In place of the particular dyes described in the foregoing examples, there may be used various other acid dyes which form salts with vinylpyridine polymers. Among the other additional useful dyes are:

	Colour Index No.
Pontachrome Black PV or Diamond Black PV	170
Pontacyl Light Green SF	670
Pontacyl Brilliant Blue A	714
Wool Violet S	50
Lithosol Red C	165

This invention has the advantage that it provides a new type of light-screening layer which may be readily prepared and is somewhat economical and effective. A further advantage is the fact that the dyes used and their light absorptive properties form an integral part of the layer and can be bodily removed with the layer. This is particularly advantageous in the case of the anti-halation layers.

The anti-halation layers of this invention are not dissolved by the alkaline developer or water-rinse baths used in the processing of a photographic element containing exposed silver halides. This means that the dyes do not contaminate the developer solutions or water-rinse baths and, hence, the solutions have greater effective life. The layers, however, can be readily solubilized by the acid present in and at the concentration used in ordinary acid processing baths, e. g., acid-stop baths, acid fixing baths, acid hardening-fixing baths, acid bleach baths, and reversal-bleach baths. The layers can be bodily removed during development if desired if an acid developing bath is used. The dye complexes have many advantages in the preparation of filter layers for multilayer film structures where their non-migratory nature prevents diffusion into and contamination of contiguous sensitized layers.

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, at least one light-sensitive silver halide emulsion layer and a light-filtering layer comprising a salt of a vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

2. A photographic element comprising a light-transmitting support bearing at least one light-sensitive silver halide emulsion layer on one surface of the support and on the other surface of the support an anti-halation layer comprising a salt of a vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

3. A photographic film element comprising a transparent film base bearing a gelatino silver halide panchromatic emulsion layer on one surface thereof and on the opposite surface an anti-halation layer comprising a salt of a vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

4. A photographic element comprising a support, at least one light-sensitive silver halide emulsion layer and a light-filtering layer comprising a salt of a polyvinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

5. A photographic element comprising a light-transmitting support bearing at least one light-sensitive silver halide emulsion layer on one surface of the support and on the opposite surface of the support an anti-halation layer comprising a salt of a polyvinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

6. A photographic film element comprising a transparent film base bearing a gelatino silver halide panchromatic emulsion layer on one surface thereof and on the opposite surface an anti-halation layer comprising a salt of polyvinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

7. A photographic element comprising a support, at least one light-sensitive silver halide emulsion layer and a light-filtering layer comprising a salt of a poly-2-vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

8. A photographic element comprising a light-transmitting support bearing at least one light-sensitive silver halide emulsion layer on one surface of the support and on the opposite surface of the support an anti-halation layer comprising a salt of a poly-2-vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

9. A photographic film element comprising a transparent film base bearing a gelatino silver halide panchromatic emulsion layer on one surface thereof and on the opposite surface an antihalation layer comprising a salt of a poly-2-vinylpyridine polymer which is insoluble in water but soluble in 1% aqueous acetic acid with an acid dye, said dye being absorbent of light rays to which the emulsion layer is sensitive.

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