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PHOTOGRAPHIC ELEMENTS HAVING A LIGHT-SENSITIVE SILVER HALIDE LAYER AND A STRIPPING LAYER COMPOSED OF A POLYVINYL PYRIDINE QUATERNARY SALT AND PROCESS OF USING SUCH ELEMENTS

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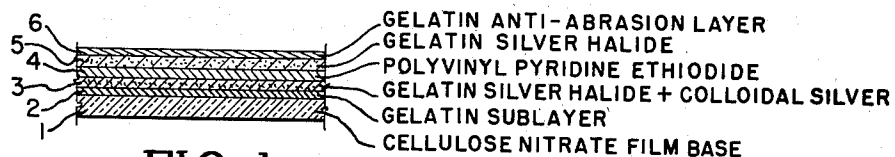


FIG. 1.

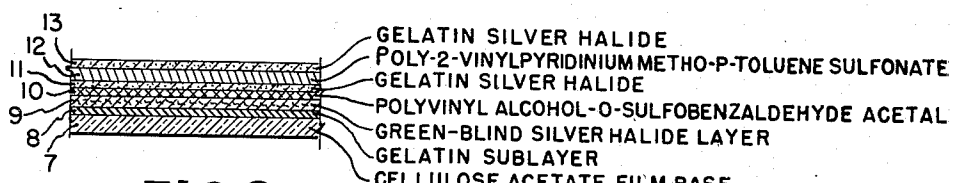


FIG. 2.

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PHOTOGRAPHIC ELEMENTS HAVING A LIGHT-SENSITIVE SILVER HALIDE LAYER AND A STRIPPING LAYER COMPOSED OF A POLYVINYL PYRIDINE QUATERNARY SALT AND PROCESS OF USING SUCH ELEMENTS

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21 Claims. (Cl. 95—2)

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This invention relates to photography and more particularly to photographic elements including films, plates and papers which bear at least one light-sensitive silver halide layer which is adhesively joined to the support or to another colloid silver halide emulsion layer on a support by means of a stripping layer composed of a polyvinyl pyridine quaternary salt. The invention also relates to a process for transferring an image-bearing layer or layers from the above stripping elements to another support.

An object of this invention is to provide a new photographic stripping element. A further object is to provide photographic stripping films. Another object is to provide multilayer photograpic films which can be individually separated from each other at different stages during processing. A further object is to produce such elements whereby the stripping action can be controlled by the use of aqueous treating baths. Another object of the invention is to provide a method for insolubilizing a polyvinyl pyridine quaternary salt stripping layer and resolubilizing it so stripping can be accomplished. A still further object is to provide a simple, economic method for delaying the stripping action of a film having a polyvinyl pyridine quaternary salt stripping layer. Still other objects will be apparent from the following description of the invention.

It has been found that photographic stripping elements can be prepared by using as the stripping layer or stratum a water-soluble polyvinyl pyridine quaternary salt. These salts adhere to a film base such as a cellulose derivative, e. g., cellulose acetate or cellulose nitrate, cellulose acetate propionate, cellulose acetate butyrate, superpolymers, e. g., nylon and polyesters, e. g., ethylene glycol-terephthalic acid polymers; metal foils, papers, e. g., baryta coated paper or to such supports which have a thin anchoring substratum composed of a water-permeable colloid e. g., gelatin. A light-sensitive water-permeable colloid silver halide emulsion layer can then be coated onto the polyvinyl pyridine quaternary salt layer and has good adherence to it. The light-sensitive silver halide layers, however, can be readily removed from the support or supporting layer by treating the element in an aqueous bath and then stripping off the latter.

The adherence of the stripping layer to the support and light-sensitive layer or water-permeable membrane bearing a colloid silver halide emulsion layer can be modified in various manners whereby one can obtain control over the stripping action.

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It has been found that polyvinyl pyridine quaternary salt stripping layers can be insolubilized and thereby converted to non-stripping layers or rendered quite difficult to strip by treating them with an aqueous solution containing a water-soluble anionic wetting agent. Suitable agents of this type include the sodium, potassium and ammonium salts of decyl, dodecyl, tetradecyl, hexadecyl, octadecyl and oleyl sulfate and the triethanolamine, triethylamine, cyclohexylamine, pyridine and tetraethyl ammonium salts of such sulfates. The insolubilized layers can be resolubilized by treatment with an aqueous solution containing water-soluble cationic surface-active wetting agent containing an aliphatic hydrocarbon radical of 8 to 20 carbon atoms, e. g., dodecyl, pyridinium chloride, cetyl pyridinium chloride, octyl-, decyl-, dodecyl-, and octadecyldimethylbenzylammonium chloride and cetyldimethylbenzylammonium chloride. The insolubilizing treatment can be effected prior to formation of the layer but in the preferred form of the invention is effected after the photographic stripping element is made and exposed and before or after development or fixation but prior to any extended washing in water.

The anionic surface-active wetting agents apparently enter into a metathetical or double decomposition reaction with the polyvinyl pyridine quaternary salt whereby the anion of the latter salt is replaced by the anion of the anionic surface-active wetting agent and the resulting polyvinyl pyridine quaternary salt is markedly less water-soluble than that of the original polyvinyl pyridine salt. The resolubilizing action takes place along similar lines and a water-soluble polyvinyl pyridine quaternary salt is later regenerated.

Various water-soluble polyvinyl pyridine quaternary salts can be used as stripping layers of the above photographic elements. Among the useful salts are the poly-N-alkylvinylpyridinium chlorides, bromides and iodides, polyvinyl pyridinium methyl-p-toluene sulfonates, polyvinyl pyridinium metho-methylsulfates and the polyvinyl pyridine etho-ethylsulfates.

The preparation of the poly-N-alkylvinylpyridinium chlorides, bromides and iodides can be accomplished by reacting an alkyl bromide, chloride or iodide with a solution of a polyvinyl pyridine, e. g., by reacting ethyl bromide with the polymeric vinylpyridine dissolved in an inert solvent such as alcohol. Detailed methods for preparing such compounds are described in Richards U. S. Patent No. 2,487,829.

The polyvinyl pyridinium metho and etho

methyl and ethyl sulfates and the polyvinyl pyridinium metho-p-toluene sulfonates are preferred polyvinyl pyridine quaternary salts because they have less effect upon the light-sensitivity of the colloid silver halide emulsion layers in the elements. The preparation of the latter quaternary salt is described in Australian application 14,741/47 and U. S. Patents 2,484,420 and 2,484,430.

The preparation of various polyvinyl pyridines useful for making the quaternary salts used in accordance with this invention as stripping layers is described in Schulze U. S. Patent 2,448,552. The polyvinyl pyridine quaternary salts from 2-vinylpyridine and 4-vinylpyridine polymers are preferred.

The vinylpyridine polymer quaternary salt layers which have been insolubilized by the foregoing treatment can be modified so that they again become quite water sensitive or water-soluble by treating the film element containing the insolubilized vinylpyridine polymer quaternary salt layer in an aqueous solution containing a cationic surface active wetting agent. The layer so modified can then be readily stripped from the remaining strata and support.

The stripping procedure can be combined with a transfer operation to a gelatin blank or other type of blank film. Hence an important aspect of the invention is concerned with a combination of the steps of insolubilizing the vinylpyridine polymer quaternary salt layer, resolubilizing such layer and stripping the light-sensitive silver halide emulsion layer carried by the stripping layer from the support or remaining layers carried by the support. The stripping operation as previously mentioned can be combined with a transfer operation whereby the image-bearing layer can be transferred to a new support.

The above procedures are applied to the film elements after they have been exposed and contain images (latent images) and can be carried out either before or after development. When the film element contains two or three light-sensitive silver halide layers they may be developed before the stripping operation is carried out. In this way all latent images are developed in one bath. When the stripping and transfer operation is conducted prior to development the separate layers can then be individually developed.

A further aspect of the invention is concerned with novel stripping films which have three light-sensitive silver halide layers and two different types of stripping layers between different light-sensitive colloid silver halide emulsion layers, one of the stripping layers being composed of a quaternary salt of a vinylpyridine polymer and the other a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups as the polymer-forming units with an aldehyde containing a solubilizing group taken from the class consisting of —COOZ and —SO_3Z, where Z is a member taken from the group consisting of hydrogen and water-soluble salt forming cations which aldehyde is otherwise unsubstituted. The stripping layers are disposed adjacent to light-sensitive silver halide layers which are to be removed.

In the multilayer films just described the stripping layers may be in either order. The processing baths however will have to be modified in accordance with the desired stripping sequence.

This is so because the cationic surface active wetting agents which solubilize the polyvinylpyridine quaternary salt layers, for example, have an insolubilizing action on the water soluble macromolecular acetal stripping layers. The procedures will be further explained below.

The preparation of certain polyvinylpyridine quaternary salts will now be described.

PROCEDURE I

Poly-2-vinylpyridine ethiodide

A sample of poly-2-vinylpyridine prepared as described in U. S. P. 2,448,552 was mechanically pulverized to a fine powder. Then 210 grams (2.0 moles) of the powder was placed in a suitable vessel with 1024 grams (6.57 moles) of ethyl iodide. The mixture was stirred until the powder had almost entirely dissolved; and it was then refluxed for four days on the steam bath. The resulting yellow solid was pulverized and washed extensively with ether and dried in a vacuum desiccator. A yield of 392 grams was obtained.

Analysis: Calculated for 100% quaternization: I, 48.7; found: I, 38.15, 38.23 indicating the degree of quaternization was approximately 59.4%.

PROCEDURE II

Poly-4-vinylpyridine ethiodide

A 10.5 gram (0.10 mole) sample of powdered poly-4-vinylpyridine (prepared in a manner similar to that described in U. S. P. 2,448,552) was dissolved in 500 milliliters of absolute methanol. (The poly-4-vinylpyridine employed was of moderately high molecular weight, having a viscosity for a 1% methanol solution of 3.8 centipoises.) To the methanol solution was added 7.8 grams (0.05 mole) of ethyl iodide. The mixture was then refluxed for four days without separation of a solid. The solution was then diluted with ether until a volume of two liters was reached; at this point the poly-4-vinylpyridine ethiodide separated as a pale yellow solid. The solid was filtered off, washed with dry ether and dried in a vacuum desiccator. The material was originally hygroscopic, but once it had been completely dried, it appeared to be unaffected by atmospheric moisture. The yield amounted to 16 grams of a lemon yellow solid (88% of theory, based on 50% conversion to the quaternary salt).

Analysis: Calculated for 50% quaternization: I, 34.7; found: I, 31.94 and 31.61 indicating the degree of quaternization was approximately 43.2%.

PROCEDURE III

Poly-4-vinylpyridine ethiodide

A 10.5 gram (0.10 mole) sample of powdered poly-4-vinylpyridine (prepared in a manner similar to that described in U. S. P. 2,448,552) was dissolved in 500 milliliters of absolute methanol. To the solution was added 62.4 grams (0.40 mole) of ethyl iodide. (This represents a 300% excess.) The mixture was heated on the steam bath for four days; at the end of this time the ethiodide quaternary salt had separated as a yellow gummy solid. The alcohol was decanted and the material mechanically removed from the flask by means of a stainless steel rod. The tacky solid thus obtained was suspended in ether, the ether was decanted and the solid was pulverized and rewashed with ether. After drying in a

vacuum desiccator there was obtained 24.5 grams of crystalline solid.

Analysis: Calculated for 100% quaternization: I, 48.7; found: I, 44.74 and 44.87 indicating the degree of quaternization was approximately 82.5%.

The preparation and processing of film elements will now be described but the invention is not intended to be limited by such examples.

EXAMPLE 1

A cellulose nitrate film base 1 as shown in Fig. 1 of the drawing having a thin gelatin substratum 2 was coated with a gelatin silver iodobromide emulsion which had admixed therewith 50% (by weight based on the silver salt) of yellow colloidal silver prepared as described in U. S. P 2,462,503, to a weight of 52 mg. silver halide per square decimeter and the resulting layer 3 was dried.

Ten (10) grams of polyvinyl pyridine ethiodide prepared in accordance with Procedure I above and having one-half of the tertiary amino groups quaternized was added to 300 ccs. of distilled water, 2.5 grams of low viscosity polyvinyl alcohol (99% hydrolyzed polyvinyl acetate), 13.3 ccs. of 5% saponin solution and additional distilled water was added until a total of 633 grams of water were present. There was then added sufficient 1N NaOH to raise the pH to 7.0±0.1. The resulting solution was coated onto the silver halide emulsion layer 3 to a weight of 20–30 mg. of dry polyvinyl pyridine ethiodide per square decimeter and the layer 4 dried.

A gelatino-silver iodobromide emulsion containing 1,1'-diethyl-2,2-cyanine iodide as an ortho-sensitizing dye was coated on the polyvinyl pyridine ethiodide layer to a weight of approximately 48 milligrams silver halide per square decimeter and the resulting layer 5 was dried. A gelatin solution containing 450 grams of gelatin per 14,400 grams of water was coated in like manner to form a thin anti-abrasion layer 6. This film element is suitable for the front film of a bipack.

The front film just described was exposed on a standard negative sensitometer, developed for a period of 15 minutes in an aqueous solution made by admixing the following components:

Water (125° F.)	cc.	750.0
N-methyl-p-aminophenol sulfate	grams	0.8
Sodium sulfite (desiccated)	do	90.0
Hydroquinone	do	1.0
Borax	do	3.0

Cold water to make 1.0 liter.

fixed without rinsing for a period of 15 minutes in a solution made by admixing the following ingredients:

Water (120° F.)	cc.	850.0
Sodium thiosulfate	grams	300.0
Sodium sulfite (desiccated)	do	11.0
Acetic acid (glacial)	do	17.0
Potassium alum	do	10.0

Cold water to make 1.0 liter.

washed in water at 60° F. for a period of 10 minutes and immediately dried, soaked for 90 seconds in a bath A (containing 25 grams of sodium dodecyl sulfate dissolved in 1000 ccs. of distilled water and adjusted to pH2 with HCl), maintained at a temperature of 70 to 72° F. The outer gelatin layer was then rolled in contact with a gelatin coated blank film (made by coating a cellulose nitrate film base to a weight of 70 mg. of dry gelatin per square decimeter from the following solution:

	Per cent
Gelatin	4.60
Chrome alum aqueous solution (10%)	0.80
Saponin	0.02
Water	94.58

the solution being adjusted to pH 4.7 with sulfuric acid before coating).

The two gelatin layers of the multilayer film and blank film were left in contact for a period of 60 seconds and then separated. The silver halide emulsion layer readily separated and had strong adherence to the blank film. The sodium dodecyl sulfate promoted anchorage between the gelatin surface of the blank film and the gelatin surface of the stripping film. There was no noticeable insolubilization of the polyvinyl pyridine stripping layer because of a lack of penetration through the outer gelatin layer of the film.

EXAMPLE 2

A film element similar to that described in Example 1 was prepared except that in place of the polyvinyl pyridine ethiodide, which was 50% quaternized, there was substituted an equivalent amount of a completely quaternized polyvinyl pyridine ethiodide, exposed, developed, fixed, washed and dried and then processed as described in that example. Similar results were obtained.

EXAMPLE 3

A film element identical to that described in Example 1 was prepared, exposed and processed in a similar manner except that it was soaked for a period of six minutes in the sodium dodecyl sulfate solution instead of 90 seconds. Due to the insolubilization of the polyvinyl pyridine layer it was not possible to successfully strip the outer emulsion layer in spite of the firm anchorage between such emulsion layer and the gelatin blank film.

EXAMPLE 4

A film element identical to that described in Example 2 was prepared, exposed, developed, fixed, washed and dried and then processed as described in that example except it was soaked for a period of 12 minutes in the sodium dodecyl sulfate bath. It was found that this soaking period insolubilized the polyvinyl pyridine ethiodide layer and prevented a successful stripping operation.

EXAMPLE 5

A film element identical with that described in Example 1 above and processed in a similar manner except that 25 grams of sodium tetralin sulphonate were substituted for the sodium dodecyl sulfate in the example. Due to the greater migrating power of sodium tetralin sulfate, the polyvinyl pyridine ethiodide layer became highly insolubilized and a successful stripping action could not be obtained.

Similar results were obtained by using the film element described in Example 2.

EXAMPLE 6

A film element of the type described in Example 1 was prepared, exposed, developed, fixed, washed and dried as described in Example 1. The film was then soaked for a period of 10 minutes in bath A (see Example 1). This film was

cut into strips (*a*) and (*b*) which were treated as follows:

(*a*) Soaked for 10 minutes in distilled water adjusted to pH 2 with HCl.

(*b*) Soaked for 10 minutes in 2.5% aqueous dodecyl trimethyl ammonium bromide adjusted to pH 2 with HCl.

The polyvinyl pyridine layer in strip (*a*) was made quite insoluble and no successful stripping action was obtained. Strip (*b*), however, was solubilized. It was soaked in bath A for a period of 30 seconds and then rolled in contact with a gelatin blank film as described in Example 1. The outer gelatino silver halide emulsion layer readily stripped from the remaining emulsion layer of the original front film and was transferred to the gelatin blank film and had excellent adherence thereto. Similar results were obtained by substituting the film of Example 2.

EXAMPLE 7

A multilayer film of the type described in Example 1 was exposed, developed, fixed, washed and dried as described in that example. It was then soaked for ten minutes in bath A and the polyvinyl pyridine ethiodide layer was made highly insoluble. The insolubilized film element was cut into strips (A) and (B) which were treated as follows:

(A) Soaked for two minutes in an aqueous solution of 25 grams di-o-tolyl guanidine base in one liter of distilled H_2O adjusted to pH 2 with HCl. The insolubilized strip layer was quickly resolubilized. Emulsion transfer was accomplished by soaking the resolubilized film in anchoring bath A for 30 seconds, rolling in contact with blank film and transferring.

(B) Soaked for two minutes in distilled H_2O adjusted to pH 2 with HCl. No resolubilizing occurred even when the soaking time was extended to 30 minutes.

Similar results were obtained by processing the film of Example 2 in like manner.

EXAMPLE 8

A cellulose acetate film base **7** as shown in Fig. 2 of the drawing having a thin gelatin anchoring substratum **8** was coated with a green-blind, red-sensitive gelatin silver iodobromide emulsion, containing the dye of Example IV of U. S. Patent 2,330,791 as the sensitizing dye, to a weight of 65 milligrams silver halide per square decimeter and the resulting layer **9** was dried. After drying, a solution containing 50 grams of a polyvinyl acetal per 1000 grams of ethanol, obtained by heating the mixture 45 minutes at 125° F. and cooling to 90° F., was coated on the emulsion layer to form a layer **10** which had a thickness of 0.0001 inch. This acetal was prepared by stirring a mixture of 44 parts of 100% hydrolyzed polyvinyl acetate (medium viscosity molecular weight 15,000 to 20,000), 40 parts of glacial acetaic acid, 40 parts of sodium-o-benzaldehyde-sulphonate-monohydrate and 6 parts of 85% phosphoric acid at 75° C. to 80° C. for one to two hours. The product is then precipitated by the addition of 1000 parts each of acetone and dried to give 75 parts of the polyvinyl acetal in the form of a white solid. A gelatino silver iodobromide emulsion layer **11** containing 1,1'-diethyl-2,2'-cyanine iodide as an ortho-sensitizing dye was coated on the polyvinyl acetal layer **10** to a weight of 60 milligrams silver halide per square decimeter. A layer **12** of poly-2-vinylpyridinium metho-p-toluene sulfonate was coated onto the ortho silver halide emulsion layer **11** from a solution containing 3 grams of the quaternary salt in 100 cc. of water to a thickness of 3 microns.

A gelatino silver iodobromide emulsion which had admixed therewith 50% (by weight based on the silver halide) of yellow colloidal silver prepared as described in U. S. P. 2,462,503, was coated onto the polyvinyl pyridine salt layer **12** to form layer **13** having a weight of 50 milligrams of silver halide per square decimeter.

Differential stripping of the film element just described is obtained as follows:

(1) Soak film for 2 minutes in solution C.

Solution C.

25.0 grams sodium dodecyl sulfate,
25.0 grams sodium tetralin sulfonate,
16.0 grams citric acid, and
5.0 grams monosodium dihydrogen phosphate monohydrate.
Distilled H_2O added to make 1.0 liter.
4 cc. 85% phosphoric acid to make pH 2.

(2) Roll in contact with gelatin blank film.

(3) Strip apart with resultant transfer of outer two emulsion layers to the gelatin blank film.

(4) Wash gelatin blank film carrying two outer emulsion layers to remove insolubilizing sodium tetralin sulfonate from cationic strip layer (about 6 minutes required).

(5) Roll in contact with gelatin blank film either directly or immediately after 30 seconds in anchoring bath A (see Example 1).

(6) Strip apart with resultant transfer of one emulsion layer.

The positions of the green and red sensitive layers in the photographic film of this example can be changed in order if desired with similar results.

EXAMPLE 9

A film element of the kind described in Example 8 was soaked for one minute in a resolubilizing bath made by dissolving 25 grams of di-o-tolyl guanidine in one liter of water and adding concentrated hydrochloric acid to a pH 2 (solution D) instead of washing for six minutes in water as described in step (4) of that example with analogous results except that the resolubilizing action was more rapid.

EXAMPLE 10

A film element like that of Example 9 except in place of the yellow colloidal silver used in the filter layer there was substituted the yellow filter dye described in U. S. Patent 2,274,782. The yellow filter dye was found to be strongly concentrated in the layer of polyvinyl pyridine quaternary salt apparently because it was a strongly charged acid dye. The film element was exposed, developed, fixed, washed and dried as in Example 1 and then processed as follows:

(1) Soaked in water or solution C (Example 8) for 3 minutes.

(2) Rolled into contact with the gelatin surface of a gelatin blank film

(3) Stripped apart, thus transferring the two outer image bearing silver halide emulsion layers to the support for the gelatin blank.

(4) The gelatin blank film with the two adherent image bearing layers and interrelated vinylpyridine polymer salt layer is then soaked in a solution D (Example 9) for 2 minutes thus

resolubilizing the vinylpyridine polymer salt layer.

(5) Soaked in bath A (Example 1) for 90 seconds.

(6) Rolled in contact with a gelatin blank film.

(7) Stripped with the resultant transfer of one image bearing layer to the new support.

The stripping film described in Example 9 and similar films need not have the polyvinyl acetal stripping layer wholly composed of such acetals. However, these polymers should constitute the essential and predominant part of the stripping layers. There may be mixed with one or more of such acetals water soluble or hydrophilic hydroxyl polymers, e. g., polyvinyl alcohol of low, medium or high viscosity, or partially hydrolyzed vinyl esters, polyvinyl acetate and polyvinyl chloracetate, polyvinyl acetals of formaldehyde, acetaldehyde, benzaldehyde, etc., wherein there is sufficient free hydroxyl groups to confer water-soluble or hydrophilic properties. This also is true of the polymeric quaternary salt strip layers, for example, low viscosity, completely hydrolyzed polyvinyl alcohol may be mixed in suitable proportions.

Also, in place of the specific polymeric acetals of the vinyl alcohol of the above examples, there may be substituted similar acetals of other aldehydes containing carboxylic and/or sulfonic acid groups. Suitable additional aldehydes include aliphatic sulfoaldehydes of the formula $HSO_3(CH_2)_nCHO$, where n is 2 to 10, e. g., beta-sulfopropionaldehyde, aliphatic carboxyaldehydes of the formula $HOOC(CH_2)_nCHO$, where n is 2 to 10, e. g., beta-formylpropionic acid; benzaldehyde-parasulfonic acid, terephthalaldehydic acid, p-(beta-formylethyl)-benzoic acid and o-carboxymethoxybenzaldehyde.

Films containing two or more stripping layers composed of the same or different polyvinyl pyridine salts of the above type can be made in accordance with the invention.

In place of the gelatin used for the binding agent for the silver halide grains, there may be substituted other hydrophilic colloids, e. g., agar agar, polyglycuronic acids, zein, collodion, water-soluble cellulose derivatives such as substantially hydrolyzed cellulose acetate, cellulose esters of hydroxy monocarboxylic acids, e. g., lactic or glycolic acids, alkali metal salts of cellulose esters of dicarboxylic acids such as phthalic acid, polyvinyl alcohol, and partially hydrolyzed polyvinyl acetate and interpolymers thereof with unsaturated materials such as styrene, maleic acid, etc., water-soluble polyvinyl acetals and other hydrophilic synthetic or natural resins and polymeric compounds. Suitable hydrophilic colloids of the above type are described in United States Patents 2,110,491, 2,276,322, 2,276,323, 2,286,215, and 2,211,323.

The present invention has the advantage that it provides a novel and practical method of temporarily insolubilizing a water-soluble stripping layer. This temporary insolubilization is of importance in commercial photographic processing laboratories in that it permits one to carry out the stripping operation in a different room from that in which the chemical photographic processing, e. g., developing and fixing, is carried out.

This means that the equipment used in the stripping operation will be free from the corrosive and toxic conditions which are present in developing rooms.

A principal advantage of the insolubilization treatment is that differential separation of a double stripping film is readily obtained. A wetting agent which increases the solubility of anionic polyelectrolyte strip layers decreases the solubility of cationic polyelectrolyte strip layers

A further advantage of the invention is that it gives the technician more latitude in the stripping operation. The stripping speed can be controlled at the will of the technician. Hence, if a certain area of a film needs a special treatment this can be readily accomplished since the stripping rate can be varied without interfering with the development operation. Moreover, the stripping operation can be carried out under well-illuminated conditions thus permitting the operator to carefully follow the stripping of each frame.

An additional advantage in the invention is that complete processing of the front film can be accomplished while retaining adherence between the image-bearing records. A master positive print of the two superposed records can be made before removing the outer record. Hence, this record can be reformed from the master positive print in the event of damage or loss of the outer layer during transferring it to another base, and stripping. A further advantage is that the stripping operations can be carried out at a central laboratory while production companies on location can process and view each day's exposures and edit them before stripping.

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 stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support, a layer composed essentially of water-soluble quaternary salt of a vinylpyridine polymer on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said polymer layer.

2. A photographic stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support, a water-soluble polyvinylpyridine quaternary salt layer on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said salt layer.

3. A photographic stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support, a water-soluble poly-2-vinylpyridine quaternary salt layer on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said salt layer.

4. A photographic stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support, a water-soluble polyvinylpyridine ethiodide layer on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said salt layer.

5. A photographic stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support, a water-soluble polyvinylpyridine alko alkylsulfate wherein the alkyl group contains from 1 to 2 carbon atoms on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said salt layer.

6. A photographic stripping film comprising a hydrophobic flexible support, a hydrophilic colloid silver halide emulsion layer on the support.

a water-soluble polyvinylpyridine alkyl-p-toluene sulfonate wherein the alkyl group contains 1 to 2 carbon atoms on said emulsion layer and a light-sensitive colloid silver halide emulsion layer on said salt layer.

7. A photographic element comprising a transparent flexible film base bearing in order on one surface a light-sensitive hydrophilic colloid silver halide emulsion layer which is predominantly sensitive to blue light, a layer composed essentially of a water-soluble quaternary salt of a vinylpyridine polymer on said emulsion layer and a light-sensitive hydrophilic colloid silver halide layer on said polymer layer, said element containing a stratum of a yellow filtering material having good blue light absorption characteristics.

8. A photographic element comprising a transparent flexible film base bearing in order on one surface a light-sensitive hydrophilic colloid silver halide emulsion layer which is predominantly sensitive to blue light, a layer composed essentially of a water-soluble quaternary salt of a polyvinylpyridine on said emulsion layer and a light-sensitive hydrophilic colloid silver halide layer on said polymer layer, said element containing a stratum of a yellow filtering material having good blue-light absorption characteristics.

9. A photographic stripping film comprising a hydrophobic flexible support bearing in order a hydrophilic colloid silver halide emulsion layer, a water-soluble polyvinylpyridine quaternary salt layer, a light-sensitive colloid silver halide emulsion layer, a water-soluble polyvinylpyridine quaternary salt layer and a light-sensitive colloid silver halide emulsion layer.

10. A photographic element comprising a hydrophobic flexible film base bearing in order on one surface a light-sensitive silver halide emulsion layer, a stripping layer composed of a polymeric material, a hydrophilic colloid silver halide emulsion layer, a stripping layer composed of a polymeric material, and a light-sensitive colloid silver halide emulsion layer, said emulsion layers being differentially sensitized so that they collectively absorb light throughout the visible spectrum, one of said polymeric materials consisting essentially of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups as polymer-forming units with an aldehyde containing a solublizing group taken from the class —COOZ and —SO_3Z, where Z is a member taken from the group of hydrogen and a water-soluble salt-forming cation, which aldehyde is otherwise unsubstituted, and the other polymeric material is a water-soluble quaternary salt of a vinylpyridine polymer.

11. A photographic element as set forth in claim 10 wherein said acetal is the sodium o-sulfobenzaldehyde acetal of polyvinyl alcohol and said quaternary salt is a poly-2-vinylpyridine quaternary salt.

12. A photographic element comprising a hydrophobic film base bearing in order on one surface a light-sensitive silver halide emulsion layer, a stripping layer consisting essentially of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups as polymer forming units with an aldehyde containing a solubilizing group taken from the class consisting of —COOZ and —SO_3Z, where Z is a member taken from the group consisting of hydrogen and a water-soluble salt-forming cation, which aldehyde is otherwise unsubstituted, a hydrophilic colloid silver halide emulsion layer, a stripping layer composed essentially of a water-soluble quaternary salt of a vinylpyridine polymer and a light-sensitive colloid silver halide emulsion layer, said emulsion layers being differentially sensitized so that they collectively absorb light throughout the visible spectrum.

13. A photographic element comprising a hydrophobic transparent film base bearing in order on one surface a gelatin anchoring substratum, a light-sensitive silver halide emulsion layer which has no sensitivity in the green region of the spectrum but has an extra range of sensitivity in the red region of the spectrum, a stripping layer consisting essentially of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups as polymer forming units with an aldehyde containing a solubilizing group taken from the class consisting of —COOZ and —SO_3Z, where Z is a member taken from the group consisting of hydrogen and a water-soluble salt-forming cation, which aldehyde is otherwise unsubstituted, a hydrophilic colloid silver halide emulsion layer which has an extra range of sensitivity in the green region of the spectrum, a layer composed essentially of a water-soluble polyvinylpyridine quaternary salt and a colloid silver halide emulsion layer containing a yellow filtering material which absorbs blue light, said layer being sensitive in blue region of the spectrum only.

14. The process which comprises exposing to a light image photographic element as described in claim 13, treating the exposed element in an aqueous solution containing a mixture of sodium dodecyl sulfate and sodium tetralin sulfonate, pressing the outermost layer of said element into contact with the gelatin layer of a gelatin blank film stripping the two image-bearing emulsion layers from the photographic element, washing the gelatin blank film carrying the two image bearing layers in water, pressing the outer image-bearing emulsion layer into contact with the gelatin layer of a second gelatin blank film and stripping said outer emulsion layer from the remaining emulsion layer whereby the three image bearing layers of the original element are disposed on separate supports.

15. A process as set forth in claim 14 wherein the washing bath contains di-o-tolyl guanidine hydrochloride.

16. A process treating an exposed photographic element comprising a hydrophobic transparent film base bearing in order on one surface a gelatin anchoring substratum, a light-sensitive silver halide emulsion layer which has no sensitivity in the green region of the spectrum but has an extra range of sensitivity in the red region of the spectrum, a stripping layer consisting essentially of a water-soluble macromolecular acetal of a hydroxyl polymer having a plurality of recurring intralinear

$$-CH_2-\underset{|}{C}HOH-$$

groups as polymer forming units with an aldehyde containing a solubilizing group taken from

the class consisting of —COOZ and —SO_3Z, where Z is a member taken from the group consisting of hydrogen and a water-soluble salt-forming cation, which aldehyde is otherwise unsubstituted, a hydrophilic colloid silver halide emulsion layer which has an extra range of sensitivity in the green region of the spectrum, a layer composed essentially of a water-soluble polyvinylpyridine quaternary salt and a colloid silver halide emulsion layer containing a yellow filtering material which absorbs blue light, said layer being sensitive in blue region of the spectrum only, in an aqueous solution containing a mixture of sodium dodecyl sulfate and sodium tetralin sulfonate, pressing the outermost layer into contact with the gelatin layer of a gelatin blank film stripping the two image-bearing emulsion layers from the photographic element, washing the gelatin blank film carrying the two image-bearing layers in water, treating the two image-bearing emulsion layers in an aqueous bath containing an alkali metal salt of an alkyl sulfate containing 8 to 22 carbon atoms, pressing the outer image-bearing emulsion layer into contact with the gelatin layer of a second blank film and stripping said emulsion layer from the remaining emulsion layer whereby the three image-bearing layers of the original support are disposed on separate supports whereby the gelatin blank film with the two adherent image-bearing emulsion layers is treated in an aqueous bath containing an alkali metal salt of an alkyl sulfate containing 8 to 22 carbon atoms before the last stripping operation.

17. A process for decreasing the water-solubility of a stripping layer of a photographic element, said stripping layer supporting a hydrophilic colloid silver halide emulsion layer and consisting essentially of a water-soluble quaternary salt of a vinylpyridine polymer, which comprises treating said salt with an aqueous solution containing an anionic wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 10 to 18 carbon atoms.

18. A process for decreasing the water-solubility of a stripping layer of a photographic elephilic colloid silver halide emulsion layer and consisting essentially of a water-soluble quaternary salt of a vinylpyridine polymer, which comprises treating said element with an aqueous solution containing a sodium alkyl sulfate of 10 to 18 carbon atoms.

19. A process for decreasing the water-solubility of a stripping layer of an exposed photographic element, said stripping layer supporting a hydrophilic colloid silver halide emulsion layer and consisting essentially of a water-soluble quaternary salt of a vinylpyridine polymer, which comprises treating said element with an aqueous solution containing a sodium alkyl sulfate of 10 to 18 carbon atoms

20. A photographic stripping and transfer process which comprises treating an exposed photographic film element comprising a film base having super-imposed thereon two latent image-bearing gelatino silver halide emulsion layers which are separated by a stripping layer consisting essentially of water-insoluble quaternary salt of a vinylpyridine polymer with an anionic surface active wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 10 to 18 carbon atoms which comprises treating said element in an aqueous bath containing a cationic surface-active wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 8 to 20 carbon atoms, pressing the outer image-bearing layer of said element into contact with the gelatin layer of a blank film comprising a transparent-film support and a gelatin layer, and stripping the image-bearing layer adhering to said gelatin layer from the remainder of the exposed photographic film.

21. A photographic stripping and transfer process which comprises treating an exposed photographic film element comprising a film base having super-imposed thereon two latent image-bearing gelatino silver halide emulsion layers which are separated by a stripping layer consisting essentially of water-insoluble quaternary salt of a vinylpyridine polymer with an anionic surface active wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 10 to 18 carbon atoms which comprises treating said element in an aqueous bath containing a cationic surface-active wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 8 to 20 carbon atoms, treating the resulting element for a short period in an aqueous anchoring bath containing an anionic wetting agent wherein the hydrophobic group is an aliphatic hydrocarbon radical of 10 to 18 carbon atoms and having a pH of 1 to 4.5, pressing the outer image-bearing layer of said element into contact with the gelatin layer of a blank film comprising a transparent-film support and a gelatin layer, and stripping the image-bearing layer adhering to said gelatin layer from the remainder of the exposed photographic film.

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