

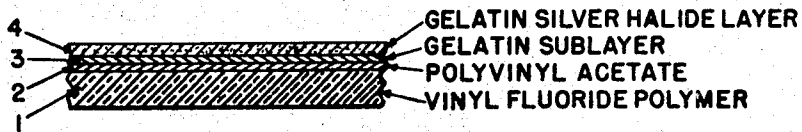
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P. R. AUSTIN

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PHOTOGRAPHIC ELEMENTS COMPOSED OF ORIENTABLE VINYL FLUORIDE POLYMERS

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INVENTOR.

PAUL ROLLAND AUSTIN

BY

Lynn B. Morris

ATTORNEY

UNITED STATES PATENT OFFICE

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PHOTOGRAPHIC ELEMENTS COMPOSED OF ORIENTABLE VINYL FLUORIDE POLYMERS

Paul Rolland Austin, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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1 Claim. (Cl. 95—9)

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This invention relates to new photographic elements which comprise a support composed of an orientable vinyl-fluoride polymer bearing a stratum of a radiation-sensitive material. More particularly, it relates to photographic film elements which comprise a support composed of an orientable vinyl-fluoride polymer bearing at least one water-permeable colloid layer which contains a light-sensitive silver halide.

Numerous materials have been proposed for use as the supports or base for photographic films. The materials which have been most widely used on a commercial scale, however, are the cellulose esters. Of these, cellulose nitrate has been generally used for cinematographic films, but has several distinct disadvantages. The untreated material is inflammable and often has an explosive rate of burning. The varieties which are plasticized with agents to reduce the burning rate are apt to discolor on aging. The films, moreover, are sensitive to water and lack dimensional stability. Cellulose esters of lower fatty acids are also widely used and while they are relatively noninflammable and form clear transparent films, they have high water absorption characteristics which adversely affect the dimensional stability of films made therefrom. In addition, the gelatin coated films become brittle at low humidities. Various synthetic resins have been proposed as film base but have not been used in commercial production.

An object of this invention is to provide a new and commercially practical photographic film element. A further object is to provide a clear transparent photographic film which remains permanently clear. Another object is to provide a film element which is substantially unaffected by changes in humidity and photographic processing solutions and has dimensional stability. A still further object is to provide a photographic film element which has good stiffness (viz., is not limp) but retains excellent flexibility in thin films (e. g., 0.002 to 0.01 inch thick). Still another object is to provide such an element which is of a low degree of flammability.

The photographic elements of this invention comprise a layer of radiation-sensitive material imposed on a support composed of an orientable vinyl fluoride polymer. The preferred elements are transparent flexible films comprising a radiation-sensitive water-permeable layer and a support composed of such polymers having a thickness of 0.002 to 0.01 inch. The films are further characterized by possessing good stiffness with flexibility and high dimensional stability, and are clear and transparent and are of a low degree of

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inflammability. The radiation-sensitive water-permeable layers furthermore are not adversely affected by the chemical nature of the support. The polymers, moreover, when heated at normal pressure have a softening point above 150° C.

The supports can be made by depositing a vinyl fluoride polymer from a solvent solution onto a hot smooth surface such as a casting wheel, band, etc., of the type used in casting cellulose derivative films. The solvent is then removed by allowing it to evaporate and withdrawing it from the casting zone.

To obtain orientable vinyl fluoride polymers as distinguished from the less desirable unorientable polymers which do not have the required strength and toughness for good film base a mixture of vinyl fluoride and from 0.005 to 5% by weight (based on the vinyl fluoride) of an organic peroxy compound is subjected, in a reaction vessel, to a pressure of at least 150 atmospheres at a temperature of 30 to 250° C. for a period of several hours. Detailed methods of preparing the orientable vinyl fluoride polymers are described in Coffman & Ford copending application, Serial Number 510,966, filed November 19, 1943. A representative practical procedure follows:

Procedure A

A stainless steel reaction vessel capable of withstanding a pressure in excess of 1000 atmospheres and provided with heating and cooling devices is swept with oxygen-free nitrogen and charged with 200 parts of deoxygenated water and 0.2 part of benzoyl peroxide which occupy about 1/4 of the total volume of the vessel. It is then closed, the nitrogen is removed by evacuation, and 100 parts of vinyl fluoride monomer containing 20 P. P. M. of oxygen and a trace of acetylene (less than 50 parts per million) is admitted. The vessel is fitted with temperature and pressure recording and controlling instruments, and is connected to a storage vessel containing monomeric vinyl fluoride of the same purity. The reaction vessel is placed in reciprocating agitator and heating and agitation are begun. When the temperature within the reactor reaches 78° C. additional vinyl fluoride is admitted from the storage vessel to raise the pressure in the system to 250 atm. Reaction sets in and the temperature is maintained at 80°, and the pressure is maintained at 250 atmospheres by addition of vinyl fluoride monomer from the storage vessel. After 15 hours the reaction is complete, 80% of the polymerization having occurred during the first two hours.

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The reactor is cooled, pressure is released, and the product is discharged. It is a friable white cake consisting of 62 parts of vinyl fluoride polymer after washing and drying. The vinyl fluoride polymer is completely soluble in hot dimethyl formamide to the extent of 10-20%, and these solutions when poured on a smooth surface and warmed to drive off the solvent give tough films, which when "quenched" by bringing to a temperature above the softening temperature and quickly cooling are clear, transparent, colorless, and remarkably free from optical graininess.

The polymers are shown to be orientable by means of a simple test. A filament or narrow strip of pressed film is subjected to longitudinal stress. It elongates up to several hundred per cent, namely, at least 100% and up to 400% or more in contrast to unorientable vinyl fluoride polymer which elongates only a few per cent until the ultimate tensile strength is exceeded and the sample breaks. The orientable polymers before orientation show X-ray diffraction patterns characteristic of a crystalline powder while after orientation by cold drawing the polymer shows an X-ray diffraction pattern characteristic of an oriented fiber.

The preparation of photographic elements from the orientable vinyl fluoride polymers is further illustrated in the following examples.

Example 1

A vinyl fluoride polymer film 0.005 inch thick prepared by casting a dimethylformamide solution containing 15% by weight of the orientable vinyl fluoride polymer described in Procedure A is subbed with a solution of 1 part of gelatin dissolved in 5 parts of 90% formic acid and 94 parts of dimethyl formamide and is dried at 100° C. It is then coated with a light-sensitive gelatin-silver halide emulsion. The resulting film dries rapidly to give a smooth, even, light-sensitive element which after exposure is processed by standard methods to a picture of excellent quality. The film before or after processing can be folded and struck sharply or bent repeatedly without breaking and the final picture shows no change in dimensions from the original unexposed element.

Example 2

A vinyl fluoride polymer film 1, as shown in the figure of the accompanying drawing which constitutes a part of this specification, of 0.005 inch thickness prepared by calendering the polymer of Procedure A is coated with a thin layer of polyvinyl acetate 2 by dipping in a 2% solution of polyvinyl acetate in 50-50 acetone dimethyl formamine and then drying at 150° C. for five minutes. The resulting film is subbed with a gelatin-acetone subbing solution to form a gelatin sublayer 3 which is then coated with a gelatin-silver halide emulsion to form a layer 4. The resulting film has, in addition to the properties possessed by the film of Example 1, an extremely high degree of adhesion between the base and gelatin coating.

Example 3

A film prepared from the vinyl fluoride polymer prepared by Procedure A above is dipped in a solution of the following composition:

	Parts
Vinyl fluoride polymer (Procedure A)	1
Dimethyl formamide	49
Nitrocellulose	2
Acetone	48

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The film after dipping is dried at 100° C. for ½ hour and subbed with the following solution:

	Parts
5 Gelatin	5
Salicylic acid	2
Water	20
Ethanol	270
Acetone	100

10 After drying for ½ hour at 60° C. the film is coated with a gelatin-silver halide emulsion and dried to yield a light-sensitive element of excellent toughness, durability, and water resistance.

The parts referred to in the above procedures 15 and examples are parts by weight.

The invention as stated above is not limited to the specific materials and embodiments set forth above. Other vinyl fluoride polymers which are capable of orientation by cold drawing (as 20 evidenced by the fact that after cold drawing they show an X-ray diffraction diagram characteristic of an oriented material) and having a softening point at atmospheric pressure above 150° C. can be used in like manner as the support for water-permeable colloid layers which are responsive to photographic processing. The vinyl fluoride polymers can be cast from solvents other than those given above. Additional solvents include tetramethylene cyclic sulfone, nitroparaf- 25 fins, e. g., nitrobutane, cyclohexanone, dibutyl ketone, mesityl oxide, aniline, phenol, methyl benzoate, phenyl acetate and diethyl phosphate.

This invention also contemplates the use of 35 interpolymers of vinyl fluoride with minor portions (20% or less by weight) of other polymerizable olefinic compounds including vinyl and vinylidene compounds, halogenated ethylene and the like. Thus the interpolymers of vinyl fluoride with 1-20% by weight of such interpolymers 40 materials as vinyl acetate, methyl methacrylate, tetrafluoroethylene, di- and tri-fluoroethylenes, ethylene, etc., can be used in preparing the light-sensitive elements of this invention. Such products being composed chiefly of vinyl fluoride have 45 properties similar to polymers prepared from pure vinyl fluoride with minor variations in solubility, stiffness, toughness, softening point, flammability, and so forth.

The film supports used in fabricating the novel 50 photographic elements of this invention are not limited to vinyl fluoride polymers alone. In general, it is unnecessary to add a plasticizer to the vinyl fluoride polymer film support, as the unmodified polymer contains all of the properties 55 desirable in a film base or support. Modifying agents such as plasticizing or softening agents may be added if desired. Suitable plasticizing agents include aromatic sulfonamides, e. g., N-methyl-p-toluenesulfonamide, N-ethyl-p-toluenesulfonamide; sulfones, e. g., tetramethylene 60 cyclic sulfone; dimethyl phthalate, diethyl phthalate, caprolactam, etc.

Various types of water-permeable colloid layers may be superposed on the vinyl fluoride polymer film supports. The water-permeable colloids 65 may contain various substances which are responsive to the development of silver salt images or to the bleaching of silver images such as dyes, dye intermediates, color formers, etc. The water-permeable colloid binding agents of the colloids may be natural or synthetic. Suitable additional colloids include the polyvinyl alcohols including the partially hydrolyzed polyvinyl acetates, and mixed polyvinyl-chloride-acetates and hydrolyzed interpolymers of vinyl acetate with un-

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saturated compounds for example, maleic anhydride, acrylic acid esters, etc. Suitable colloids of the last mentioned types are disclosed in U. S. P. 2,276,322 and 2,276,323.

Still other colloids include hydrophilic partially substituted polyvinyl esters and acetals and mixtures such as those in U. S. P. 2,245,218 and the low substituted cellulose esters of saturated aliphatic monocarboxylic acids of 2 to 4 carbon atoms and low substituted cellulose ethers, e. g., methylcellulose, ethylcellulose, benzylcellulose, etc. Among the natural colloids may be mentioned, casein, albumin, gelatin, gum arabic, agar-agar, polyglycuronic acid, etc.

Various radiation-sensitive materials may be present in the light-sensitive layers. 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. Other light-sensitive 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 only a low sensitivity to water. Thus polyvinyl acetate or a cellulose acetate may be used as the colloidal binder. Other radiation-sensitive layers, e. g., heat-sensitive layers of silver or mercurous oxide in gelatin; layers which are especially sensitive to ultra violet light, e. g., anhydride of fulgenic acid and layers of fluorescent chemicals may also be imposed on the novel supports hereof.

The water-permeable colloid layers may contain immobile or non-diffusing dye intermediates or color formers which are capable of forming quinonimine or azomethine dyes on color coupling development of silver salt images or of forming azo dyes on coupling, e. g., by an azo reversal procedure. A plurality of the above layers can be imposed on a single support. For instance, a multilayer element for 3-color photography may contain a yellow filter layer and a plurality of differentially sensitized silver halide colloid emulsion layers containing color-former nuclei or compounds which are so arranged and sensitized that they record a portion of the light in the visible spectrum. Such elements may contain an antihalation layer such as a gelatin layer containing actinic-light-absorbing dyes or pigments or colloidal silver. Water permeable colloid layers, e. g., gelatin containing removable filter dyes may also be present.

Thin coatings of other polymeric materials may be applied as surface coatings to improve the anchorage between the water-permeable photographic responsive layers and the vinyl fluoride polymer support. Materials suitable for such uses are nitrocellulose, cellulose esters, water-sensitive polyvinyl compounds, e. g., polyvinyl acetate, hydrolyzed or partially hydrolyzed polyvinyl acetate, and interpolymers of vinyl acetate with other vinyl or vinylidene compounds or terminally unsaturated olefins. A particularly desirable application of this type of coating is shown in Example 2 where a thin coating of polyvinyl acetate of less than 0.001 in. thickness is coated on the vinyl fluoride polymer. Such films may then be subbed by the same means employed with films consisting solely of the overcoating polymer. This gives excellent anchorage between the base and the colloid layer, e. g., the light-sensitive silver halide layer.

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The polyvinyl fluorides may be used to impart their desirable properties to other polymers by means of surface coatings thereby forming a laminated film element. Thus, the fire hazard of cellulose nitrate films may be substantially lowered by surface coating with a vinyl fluoride polymer. A similar surface coating of cellulose acetate film leads to a great improvement in flexibility and water resistance.

The vinyl fluoride polymer supports may be of different thicknesses depending on the use to which the finished article is to be put. In general, due to the increased toughness of such polymers much thinner films are feasible than in the case of the cellulose esters. This is a definite advantage in the case of cine film and film for aerial photography because a greater length of films can be placed in each reel, or spool.

In the case of film for medical or industrial X-ray usage, the support or a stratum on the support can be dyed or tinted blue, green, etc., to facilitate the inspection of the radiographs and/or to minimize eye strain.

The photographic films of this invention possess many outstanding advantages. They are characterized by unexpectedly high flexibility and strength, practically complete water resistance, and absence of fire hazard, a combination of properties not possessed by the nitrocellulose or cellulose fatty acid ester films. The great strength and flexibility of the present film manifests itself in the case of perforated cinematographic films in a large increase in the life of such films which are continually exposed to the wear of projection.

The flexibility and toughness of the film support of the present invention is strikingly demonstrated when measurements are made at low relative humidities. Thus, cellulose acetate film, after exposure to an atmosphere of 50% relative humidity at room temperature withstands about 15 bends in the Pfund flexometer and when bone dry, less than 10 bends. On the other hand, vinyl fluoride polymer films are not affected by 200 flexes (under either condition) and in fact, when tested on the Schopper flexometer the films stored at 50% relative humidity withstand over 9000 folds before breaking.

The high degree of flexibility and toughness is particularly evident in the case of a film coated with photographic emulsion. Thus the standard commercial, photographic films composed of cellulose esters having a gelatin silver halide coating break in two when bent sharply, between the thumb and index finger with the gelatin coating outside. The photographic films of this invention do not break although the emulsion coating when brittle may develop a crack.

The low water resistance of cellulose ester films manifests itself mainly in two ways in the preparation of light-sensitive elements. First, during the drying operation after coating, the cellulose ester film absorbs a relatively large amount of water from the emulsion, causing non-uniformities, streaks and splotches in the emulsion coat. Second, the sensitivity of cellulose esters to water leads to deformation of the film itself in coating. The films of the present invention are completely free from these defects. The dry films of this invention absorb less than 0.3% of water when placed in contact with water at 20° C. for one hour. Even when soaked for 24 hours in water, the films of this invention absorb less than 0.5% water and show practically no change in dimensions. In contrast to this, films of cellulose ace-

tate and nitrocellulose absorb about 3 to 5% of water under these conditions. Deformation during coating does not take place. The coated photographic film elements evidence no distortion or deformation and are particularly useful in the graphic arts, aerial photography and map-making where distortion of images due to linear or area changes in the film base during processing must be at an absolute minimum. As an additional advantage, the strength and stiffness of vinyl fluoride polymer film elements after soaking for 24 hours is not appreciably less than that of the dry film.

The film supports of the present invention do not evidence any hydrolysis or decomposition on prolonged treatment with water and photographic processing solutions or extended exposure to humid conditions. This fact is of extreme importance in films used in color photography where it is recognized that slow hydrolysis and decomposition of the common cellulose esters lead to a degradation of the dye intermediates or dyes employed in forming the colors. The film elements of this invention being resistant to hydrolyzing influences met with in the processing and storage of photographic film are entirely satisfactory for archival and documentary records in color.

The films of this invention, as has been pointed out above, burn with difficulty and even when placed in a flame, show none of the violent burning associated with cellulose nitrate. In most cases the film melts into globules of polymer and burns only very slowly when removed from the flame.

It will be apparent from the foregoing description that the new photographic films described herein possess a combination of properties ideally suited for all of the known photographic applications where a flexible material is employed. No limitation appears to exist upon their use in the photographic and photomechanical industries; that is, they can be used with the advantages outlined above as cut or rolled film, in amateur or

professional cinematography, the recording of documents, X-ray diagnosis, color photography, aerial photography, map-making, and sound recording.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claim.

I claim:

A flexible photographic film element comprising a transparent flexible support composed essentially of orientable polyvinyl fluoride which has a softening point above 150° C., having superposed thereon in order a thin layer of polyvinyl acetate, a sublayer of gelatin and a gelatino-silver halide emulsion layer the said thin layer of polyvinyl acetate being interunitied with the said support and the said sublayer whereby there is a high degree of adhesion between the support and gelatin coating.

PAUL ROLLAND AUSTIN.

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