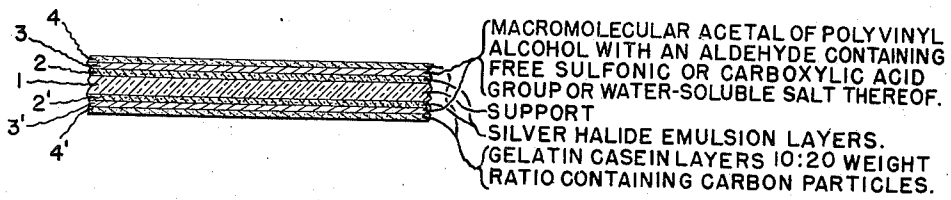
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LIGHT-SENSITIVE PHOTOGRAPHIC ELEMENT

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LIGHT-SENSITIVE PHOTOGRAPHIC ELEMENTS

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2 Claims. (Cl. 95—8)

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This invention relates to novel photographic elements which have the photosensitive layer or layers thereof protected from exposure to visible light. More particularly it relates to such elements which are useful for obtaining X-ray photographs or radiograms. Still more particularly it relates to X-ray films which can be safely handled under conditions of ordinary room illumination without exposure of the photosensitive layers thereof and yield developed radiographs free from coloring matter.

Photographic elements with various types of antihalation layers have been proposed and manufactured commercially. In general they comprise a support, a light-sensitive layer, and an antihalation layer composed of a removable natural or synthetic material which has dispersed therethrough an antihalation or light-absorbing dye or pigment. The light-sensitive layer is placed on one side of the base and the antihalation layer on the other. Various water-soluble cellulose derivatives and synthetic resins are among the substances which have been proposed. Materials which are soluble in dilute alcohol solutions or in alkaline developer solutions have also been advocated but they require special conditions for manufacturing or processing.

Photographic elements for obtaining X-ray photographs which are provided with an opaque protecting medium for the sensitive layer are known. The previous protective layers, however, were not entirely satisfactory for X-ray films because the layers were difficult to remove after exposure to X-rays and the light-blocking material is not uniformly distributed throughout the layer.

Murray United States Patent No. 2,379,373 relates to photographic elements and, more particularly, to X-ray film elements comprising a base, a light-sensitive emulsion layer, a light-blocking outer antihalation layer disposed on each side of said element composed of casein and gelatin in the proportion of 10 to 20 parts of the former per part of the latter having intimately and uniformly dispersed therethrough finely divided carbon particles. These elements, while commercially practical, sometimes have the disadvantage that complete removal of the finely divided carbon is difficult. A small amount of carbon particles sometimes becomes anchored to the photographic emulsion layer at the fusion point between the emulsion layer and the protective layer.

This invention has for an object a photographic

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element for X-rays which can be handled under daylight conditions without exposure. A further object is such an element which is provided with antihalation layers which can be removed easily and completely in aqueous baths. A still further object is to provide such an element wherein the antihalation layer is photographically inert and the light-blocking material is non-diffusing and uniformly dispersed throughout the layers. A still further object is to improve the photographic elements of the aforesaid United States patent.

The novel photographic elements or X-ray elements of this invention comprise a base having superposed thereon at least one photosensitive emulsion layer, two outer light-absorbing protective layers disposed on the outer surfaces of the elements, and a removable water-soluble colloid layer intercalated between any emulsion layer and said protective layer. In the case of duplicoated X-ray film, the elements comprise a film base or support having a photographic emulsion layer coated on each side of the base and a protective layer coated on each photographic emulsion layer which contains a non-diffusing, light-absorbing material.

The protective light-blocking or antihalation layers consist of an aqueous dispersion of a mixture of casein and gelatin and a black inert pigment such as colloidal carbon or finely divided carbon black which is uniformly distributed therethrough. The casein and gelatin are present in the amount of 10 to 20 parts of the former per part of the latter. The amount of the black inert pigment particles may vary over a fairly wide range but should be present in sufficient amount that thin layers prevent visible light from penetrating therethrough and exposing the photographic layers. A particle size of 10 to 100 mu represents a practical range and 30 to 80 mu a preferred range for aforesaid pigments.

The coating mixtures can be made in the form of an aqueous dispersion or paste and coated in a manner similar to that in which gelatin-silver halide emulsions are coated. They can be made by dispersing the colloidal silver or carbon black in an aqueous dispersion of gelatin and casein. Various wetting and dispersing agents can be used in aiding the dispersions such as sodium alkyl sulfates of 10 to 18 carbon atoms, lower alkyl naphthalene sulfonic acid alkali metal salts wherein the alkyl groups have 1 to 4 carbon atoms, e. g., tri-isopropyl naphthalene sulfonic acid sodium salt, sodium or potassium alkane sulfonic acid salts having 10 to 18 carbon atoms, etc. Coating may be accomplished by spreading,

spraying, dipping, transfer, or beading rollers, etc.

Various thicknesses of the antihalation layers may be formed but, in general, thicknesses of 15 to 50 microns in thickness are sufficient. The thickness of the layer and amount of pigment should be controlled so that the resulting layer has a density of about 4 to 7.

The removable water-soluble layers may be composed of any water-soluble colloid (viz. which has a marked solubility in water at 20° C.) of natural or synthetic type. Suitable colloids include water-soluble cellulose derivatives, e. g., low substituted cellulose ethers, such as methyl cellulose, ethyl cellulose, and benzyl cellulose, cellulose esters having solubilizing acid salt groups, e. g., sodium, potassium, and ammonium salts of cellulose acid phthalate, cellulose ether acids, e. g., sodium cellulose glycollate, casein gelatin mixtures, water-soluble synthetic resins, e. g., polyvinyl alcohol, and esters.

A preferred type of water-soluble layer is composed of a macromolecular water-soluble acetal of a vinyl alcohol polymer with an aldehyde containing a free sulfonic acid or free carboxylic acid group or an alkali metal, ammonium or amine salt of such acids. An element containing this preferred type of water-soluble layer is shown in Fig. 1 of the accompanying drawing wherein a base 1 is provided on each surface with a silver halide emulsion layer 2 and 2', a removable layer 3 and 3' composed of a macromolecular water-soluble acetal of a vinyl alcohol polymer with an aldehyde containing a free sulfonic acid or carboxylic acid group, or a water-soluble salt thereof is deposited on each emulsion layer and an antihalation layer 4 and 4' composed of gelatin and casein in the proportion of 10 to 20 parts of the former per part of the latter which has finely-divided carbon uniformly dispersed therethrough on removable layers 3 and 3'.

The water-soluble colloids can be coated from an aqueous solution or solvent mixtures which do not have a deleterious effect on the light-sensitivity of the emulsion layers. Aqueous solutions containing 5 to 45% by weight of a water-soluble alcohol, e. g., ethanol or methanol, and a small amount, e. g., 0.05 to 2% by weight of a wetting agent are preferred. From 5 to 20 grams of colloid per 100 cc. of solution constitutes a practical range. The coating may be applied by any of the methods useful in coating gelatin emulsions on supports including those referred to above.

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

Example I

A cellulose acetate film base was suitably subbed with gelatin and coated on each side with a gelatin-silver halide emulsion of the X-ray type. Each emulsion surface was coated at 75° F. with the following solution:

Methyl cellulose (1.3 to 2.6% methyl groups per glucose unit)	grams	10
Water	cubic centimeters	350
Ethanol	do	50
Sodium dodecyl sulfate (10%)	do	5

A dispersion of the following composition was prepared by mixing Solution B with Solution A and then adding Solution C with vigorous stirring.

Solution A

Water	cubic centimeters	9100
Casein	grams	1000
Sodium carbonate (10% aqueous solution)	cubic centimeters	340

Solution B

Colloidal carbon (particle size 50 mu)	grams	1000
Water	cubic centimeters	2000
Sodium dodecyl sulfate (10% solution)	do	20

Solution C

Gelatin	grams	100
Water	cubic centimeter	1250
Sodium dodecyl sulfate (10% aqueous solution)	do	100
Saponin (5% aqueous solution)	do	100

The mixture was coated onto each methyl cellulose layer at about 90° F. to form a layer approximately 30 microns thick. The above coating operations were carried out in the absence of actinic radiations. The resulting layer, after drying, had a density greater than 4.0. No visible fog was produced after a 20 minute exposure in a normally lighted room but a slight edge fog developed, e. g., about ⅜ inch around the periphery of the film. The black antihalation layers and the contiguous water-soluble colloid layers were removed easily after a three minute soak in water by gentle swabbing with cotton.

The film element as described above was exposed in the usual manner to X-ray radiations in ordinary room illumination without the use of a cassette. The film was processed as follows:

1. Developed for four minutes in a solution made by admixing the following components:

Hydroquinone	grams	7.5
p-N-ethyl-aminophenol sulfate	do	5.0
Sodium sulfite (anhydrous)	do	60.0
Sodium carbonate (anhydrous)	do	50.0
Potassium bromide	do	15.0
Water to	liters	1.0

2. Treated for one minute in a stop bath of the composition:

	Volumes
Acetic acid (28%)	1
Water	20

3. The outer black layers were then removed in water by gentle swabbing.

4. Fixed for five minutes in a solution of the composition:

Sodium thiosulfate crystals	grams	240.0
Sodium sulfite (anhydrous)	do	6.0
Boric acid	do	6.0
Potassium alum	do	12.0
Acetic acid (28%)	cubic centimeters	35.0
Water to	liters	1.0

5. Washed and dried whereby an excellent radiograph free from any surface discoloration was obtained.

Satisfactory radiographs were taken without cassettes or holders under ordinary room illumination and no loss of emulsion speed was noted.

Example II

A photographic paper composed of an interfelted white paper stock and a black pigmented paper stock forming a photographically opaque black outer stratum is provided with a baryta

coating on the white stratum upon which is deposited an X-ray sensitive gelatino-silver halide emulsion. The emulsion layer was coated at 90° F. with a solution of the following composition to a thickness of 15 microns.

Casein	grams	20.0
Water	cubic centimeters	100.0
Na_2CO_3 (20%)	do	6.8
Gelatin	grams	1.0
Mannitan monolaurate (10%)	cubic centimeters	5.0
Water	do	50.0

On the surface of the casein gelatin layer was coated a thin layer (e. g., 40 mu.) from a dispersion made by mixing the following solutions with stirring.

Solution A

Water	cubic centimeters	10,000
Casein	grams	2,000
Sodium carbonate (20% aqueous solution)	cubic centimeters	680

Solution B

Colloidal carbon (particle size 60 mu)	grams	600
Water	cubic centimeters	3000
Condensation product of ethylol cyanamide with lauric acid (1% solution)	do	2

Solution C

Gelatin	grams	100
Water	cubic centimeters	3000
Sodium dodecyl sulfate (10% solution—aqueous)	do	25
Saponin (5% solution—aqueous)	do	75

Solution B was added to Solution A slowly and then Solution C was added and the resulting solution filtered. The composition was then coated in darkness onto each of the emulsion layers of aforesaid film element to a thickness of 50 microns. The resulting element had a density of greater than 4 on either side. The layer was easily removed in the developing solution by a gentle swabbing with cotton. The element can be safely handled in daylight or under ordinary artificial illumination without exposure of the light-sensitive stratum. Upon exposure and development as in Example I, the outer layers were readily removed without leaving any residual deposit of the light-blocking layer on the film.

Example III

In place of the methyl cellulose solution of Example I was used the following:

Corn dextrine	grams	10
Water	cubic centimeters	100
Ethanol	do	20
Saponin solution	do	10
Aerosol CEL (10%)	do	2

The resulting element had properties similar to those of Example I.

Example IV

In place of the gelatin-casein coating solution of Example II was substituted:

Cellulose acetate-acid phthalate	grams	5
10% Na_2CO_3	cubic centimeters	10
Water	do	150
Ethanol	do	50
Gelatin	grams	5
Water	cubic centimeters	100

The resulting element had properties similar to those of Example I.

Example V

In place of the gelatin-casein coating solution of Example II there was substituted the following solution:

Sodium-o-sulfobenzaldehyde acetal of polyvinyl alcohol	grams	4
Ethanol	cubic centimeters	100
Water to	do	10

The resulting complete element when processed after the manner described in Example I gave similar results.

The hydrophilic macromolecular acetal described in Example V can be made by the reaction of a vinyl alcohol polymer, including interpolymers, with an aldehyde containing a sulfonic acid or carboxylic acid group or an alkali metal, ammonium, or amine salt of such acids, under acetal-forming conditions. For example, the acetalization may be conveniently carried out in solution or suspension in water or an organic solvent or diluent using a catalyst such as phosphoric acid, sulfuric acid, hydrochloric acid, etc. Suitable procedures and aldehydes are described in United States Patent 2,310,943 and in German Patent No. 643,650. The free acid groups can be converted into salt groups by a simple neutralization.

Partially and completely hydrolyzed polyvinyl alcohols of low, intermediate, and high viscosity, having a molecular weight of 5,000 to 50,000 and hydrolyzed interpolymers of vinyl esters with one or less equivalent of a terminally unsaturated interpolymerizable organic compounds can be used in preparing the vinyl alcohol acetals of aldehydes containing carboxylic or sulfonic acid groups. In general, such polymers having for each 100 carbon atoms between 20 and 50 free non-phenolic hydroxyl groups are useful.

Water-soluble, macromolecular, neutralized acetals of vinyl alcohol polymers useful in accordance with this invention are prepared by acetalization from (1) polyvinyl alcohol of high molecular weight (viscosity of 4% aqueous solution at 20° C., 40 to 60 centipoises), (2) polyvinyl alcohol of medium molecular weight (viscosity of 4% aqueous solution at 20° C., 15 to 30 centipoises) which may be substituted on 40 to 60% of the hydroxyl groups with acetate, propionate, acetal, propional, and butyral groups, and (3) 75 to 100% hydrolyzed interpolymers of vinyl acetate with 0.05 to 0.5 mol equivalents of terminally unsaturated mono-olefins, e. g., ethylene, such as described in Roland United States Patent No. 2,386,347, and (4) completely hydrolyzed interpolymers of vinyl acetate with minor portions (less than 50%) of polymerizable vinyl or vinylidene compounds, for example, vinyl chloride, vinyl cyanide, alkyl methacrylates, e. g., methyl and ethyl methacrylate, etc., with an aldehyde containing carboxylic or a sulfonic acid group.

The preferred polyvinyl acetals have the above properties and, in addition, are colorless or substantially colorless and are free from color former nuclei. The preparation of suitable such acetals for the removable layers is also more fully described in copending application Serial No. 651,996 filed March 5, 1946.

Various commercial forms of colloidal carbon or carbon black which have a very fine particle size, for instance, from 10 to 100 millimicrons, including mixtures of particles having sizes within

these ranges can be substituted for those described in the above examples. Small amounts (e. g., 0.5 to 2% of the gelatin) of the cellulose derivatives described in such patents may also be present. The black inert pigments can be used in a wide range of proportions, e. g., one part by weight of pigment to 20 parts of combined casein and gelatin to two parts of pigment to one part of combined gelatin and casein.

Additional useful wetting agents include alkali metal alkyl sulfates of 8 to 20 carbon atoms, e. g., sodium octyl sulfate, sodium tetradecyl sulfate, sodium hexadecyl sulfate, ammonium octadecyl sulfate, oleyl sulfate, sodium n-hexadecanesulfonic acid, tri-isopropyl-napththalene sulfonic acid, the condensation products of ethylol cyanimides with lauric, stearic, palmitic, etc., acids.

By varying the proportion of casein to the photographic gelatin it is possible to modify the properties of the light absorptive layers somewhat. The higher proportions, e. g., 20 to 25, of casein make the layers removable in a water rinse before development, whereas somewhat lower proportions render the layers soluble in alkaline developer solution. Proportions near the lower limits render the layers removable at the end of normal development with gentle swabbing. Water rinses after development remove all traces of the products.

The antihalation elements of this invention as described above have all the desirable characteristics of a commercially practical element. Their prepartion does not present any coating difficulties. The two outer layers are soluble in aqueous treating baths and may be readily removed from the film by treatment in such baths. They are photographically inert and hence do not adversely affect the radiation sensitive layers. The light-blocking pigments are non-diffusing and are uniformly dispersed throughout the combination colloid layer.

The invention provides a novel X-ray film which can be handled safely in diffused daylight or under ordinary room illumination but yet can be easily processed to X-ray photographs. They may be processed in ordinary illumination if so desired. They eliminate the use of cassettes and enable the technicians to exercise much greater latitude and attain more speed in roentgenology. In addition, the layers are abrasion resistant, have good anti-static properties, are not affected by usual changes in humidity, and have good aging properties.

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 base, a light-sensitive emulsion layer, an outer antihalation layer disposed on each side of said base composed of casein and gelatin in the proportion of 10 to 20 parts of the former per part of the latter, having intimately and uniformly dispersed therethrough finely divided carbon particles and a water-soluble acetal of a vinyl alcohol polymer containing a group taken from the class consisting of free sulfonic acid groups, free carboxylic acid groups, and their water-soluble salts intercalated between said emulsion layer and antihalation layer.

2. A photographic element comprising a base, a light-sensitive emulsion layer, an outer antihalation layer disposed on each side of said base composed of casein and gelatin in the proportion of 10 to 20 parts of the former per part of the latter, having intimately and uniformly dispersed therethrough finely divided carbon particles and a water-soluble sodium-o-sulfobenzaldehyde acetal of polyvinyl alcohol intercalated between said emulsion layer and anti-halation layer.

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