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3,708,302

SILVER HALIDE EMULSION SENSITIZED WITH THIOAMINE-GLUTARALDEHYDE OR ACRYLIC ALDEHYDE ADDUCT

James Plakunov and James Edward Koller, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

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8 Claims

ABSTRACT OF THE DISCLOSURE

Coating compositions comprising a hydrophilic colloid and an adduct of a first compound which is a thioamine with a second compound which is glutaraldehyde or acrylic aldehyde. The compositions when coated upon photographic materials effect a significant speed increase without detrimentally affecting the other sensitometric properties of said materials.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to radiation sensitive, image-forming materials and methods for increasing the photographic speed of said materials. In one aspect, this invention relates to a hydrophilic, water permeable overcoat for photographic materials, said overcoat having dispersed therein an adduct of a thioamine with glutaraldehyde or acrylic aldehyde. In another aspect, this invention relates to image-forming materials, such as photographic silver halide elements, and especially to high speed negative materials such as X-ray films or light sensitive material employed in making color material especially color separation negatives, containing a distinct layer comprising said adduct. In still another aspect, this invention relates to the rapid processing of high speed negative materials said material containing a distinct layer comprising said adduct.

Description of the prior art

The processing of photographic materials has for many years been performed by conventional processing methods such as tank and tray processing methods. The quality of the conventionally processed photographic material has generally been satisfactory. However, the processing time is generally long, that is, in the order of from 10 to 20 minutes. A familiar problem with respect to conventional processing techniques is the lack of reproducibility even under the most carefully controlled conditions. In the case of medical radiography, both time of processing and reproducibility can be of critical importance with respect to its use as a diagnostic technique. The radiologist should have the utmost confidence that changes appearing upon a radiograph at a later time are a manifestation of physiological changes in the patient and are not a result of processing variations. With respect to color separation, the same problems of time and variation also exist. Time can be a critical factor, for example, in the need to prepare a newspaper edition.

In recent years, the demand for fast processing and reproducibility has brought about the development of roller transport systems such as that disclosed in U.S. Pat. 3,147,090. In co-filed application entitled Novel Compositions and Photographic Processes, Ser. No. 104,690, filed by C. F. Amering, it is shown that the photographic speed with reference to development can be increased, in a photographic processing or developing solution by employing an adduct of a thioamine with glutaraldehyde. The system disclosed by Amering is particularly adapt-

able to and preferably employed in machine processing. Although it is known to add either cysteine or aldehydes to photographic systems, i.e., photographic elements and photographic developers, it has not been taught heretofore that one may incorporate into a photographic element the combination of an aminothiols with a dicarbonyl or dicarboxy compound or an α,β -unsaturated aldehyde.

U.S. Pat. 2,449,153 of Urbach issued Sept. 14, 1948, discloses photographic silver halide emulsions containing cysteine but does not suggest the use of aldehydes. Furthermore, the patent teaches that cysteine is to be added to the silver halide emulsion but does not suggest cysteine to be added to an overcoat layer.

U.S. Pat. 2,955,036 of Dersch and DeAngelus issued Oct. 4, 1960, shows that certain derivatives of cysteine can be employed as antifogging and stabilizing agents for photographic silver halide.

Aldehydes as hardeners are well known addenda for photographic system, for example, see U.S. Pats. 3,220,849 of Baden and Bard issued Nov. 30, 1965; 3,418,132 of Ketz, Jr. issued Dec. 24, 1968; and 2,247,569 of Brunken et al. issued 1941; 2,279,411 of Peterson issued Apr. 14, 1942; and 3,232,764 of Allen and Burness, issued Feb. 1, 1966.

Although the systems disclosed in the co-filed Amering application describes a developer composition which yields high quality photographic products, it would be highly desirable to eliminate the non-uniformity which may be inherent in the processing conditions. The non-uniformity can be due to the constant change, for example, of the adduct level as a result of the continuous use of the processing solution.

It has unexpectedly been discovered that by dispersing an adduct of a thioamine with glutaraldehyde or acrylic aldehyde in a hydrophilic water permeable colloid overcoat for a photographic silver halide layer one not only effects an increase in photographic speed, but, additionally, one effects an increase in speed that is uniform throughout the material regardless of the state of seasoning of the processing solutions. It is, furthermore, surprising that this improvement can be obtained whether processing is accomplished with hardening developers such as the type described in U.S. Pat. 3,147,090 or non-hardening developers. The ability to use conventional non-hardening developers in the processing of photographic elements, such as X-ray materials, is a decided advantage because of their greater stability over hardening developers. It has further been unexpectedly discovered that while the adduct can be dispersed in an overcoat for a photographic silver salt layer, the adduct will cause a serious loss in sensitometric properties when dispersed in the silver halide layer. This significant feature is unexpected since addenda employed in silver salt processing solutions are generally compatible with silver salt layers when incorporated therein. It is furthermore unexpected that the advantages of the invention are realized only when the adduct is incorporated in the overcoat since the compounds employed in the formation of the adduct are well known addenda for silver halide emulsions.

The increase in photographic speed with respect to development provides several degrees of freedom not ordinarily available, for example, one may decrease the silver halide coverage, the processing time for the exposed film can be decreased, or with regard to radiography, the patient may be exposed to small amounts of radiation.

SUMMARY OF THE INVENTION

In accordance with this invention, there are provided novel photographic elements which exhibit a marked increase in the sensitivity of the element accompanied by uniformity throughout the material upon processing in

the presence of a hardening or non-hardening developer. The photographic element comprises a support, a silver halide layer and a distinct layer containing an adduct of a thioamine with glutaraldehyde or acrylic aldehyde.

It is an object of this invention to provide means for increasing the speed of electromagnetic radiation-sensitive elements,

It is another object of this invention to provide means of processing image forming layers under constant and uniform conditions.

It is another object of this invention to provide a novel coating composition for photographic elements said composition comprising a water permeable, hydrophilic colloid having dispersed therein the adduct referred to supra.

It is still another aspect of this invention to provide novel radiation sensitive elements having increased speed without appreciably degrading contrast or minimum density.

It is yet another object of this invention to provide photographic X-ray material that can be processed in a non-hardening developer or hardening developer.

It is still another object of this invention to provide color separation materials which can be processed at increased speeds without seriously affecting the sensitometric properties of said materials.

Other objects of this invention will become obvious to those skilled in the art from that which follows.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with with this invention, the above and other objects are attained by providing a coating comprising an adduct of a thioamine with glutaraldehyde or acrylic aldehyde. In a preferred aspect, the adduct is dispersed in water permeable hydrophilic colloid vehicle. The water permeable hydrophilic coating so provided is coated over a photographic silver halide element. Thioamine should be understood to be an amine compound containing a sulfur atom having an oxidation state of two.

Illustrative of the thioamines which may advantageously be utilized are aminothiols, aminodisulfides and thio-lactones. The first of said compounds of their salts and preferably the hydrochloride salts which are preferably employed in the formation of the adducts fall into two general classes. Compounds illustrative of Class I each contain at least one sulfur atom having an oxidation state of two, a carboxy group or its lactone, and an amine group. Compounds illustrative of Class I are cysteine or its homologues and other amino acids containing a sulfur atom having an oxidation state of two. Compounds of Class II contain an amino group and a sulfur atom having an oxidation state or two. The following list is illustrative of first compounds suitably employed in forming the adduct of this invention:

Class I:

L-cysteine·HCl,
L-cystine,
DL-penicillamine,
DL-homocysteinethiolactone·HCl, and
DL-lanthionine

Class II: 2-aminoethanethiol·HCl

In a preferred aspect of this invention the first compounds employed in forming the adducts of this invention are those of Class I. In another preferred aspect cysteine, penicillamine, homocysteinethiolactone and 2-aminoethanethiol·HCl are employed as first compounds utilized in forming the adduct. In yet another preferred aspect cysteine is employed as a first compound in forming the adduct.

The second of said compounds employed in the formation of the adducts employed in this invention is a glutaraldehyde or acrylic aldehyde.

The preparation and description of the adducts employed in this invention are described in co-filed Amering application Ser. No. 104,690 entitled Novel Compositions and Photographic Processes. The adducts of a thioamine, for example cysteine, and glutaraldehyde are prepared in the same manner as the adducts described in Amering. The adducts are readily formed by adding the first compound to the second compound, or vice versa, in a suitable solvent, preferably an aqueous solvent.

Illustrative of the adducts which may be employed in this invention are the products obtained by mixing: cysteine and glutaraldehyde, glutaraldehyde and DL-penicillamine, glutaraldehyde and DL-homocysteinethiolactone, glutaraldehyde and 2-aminoethanethiol. Preferred adducts are those formed from glutaraldehyde and one of L-cysteine.HCl DL-penicillamine, DL-homocysteinethiolactone.HCl, and 2-aminoethanethiol.HCl.

The speed increases and fog levels obtained are dependent upon the amount of first compound employed in forming the adduct as well as the ratio of said first compound to said second compound. With increased use of cysteine, one obtains greater speed increases. The useful ratios of first compound to second compound can vary over a wide range, said ranges being easily determined through routine experimentation. A preferred range of ratios, in terms of moles, is from 1:1 to about 1:8 of said first compound to said second compound. Another preferred range of ratios is 1:1 to about 1:4.

In one embodiment, this invention comprises a water permeable coating composition comprising a hydrophilic colloid and the adduct.

The hydrophilic colloid vehicles for said adduct can include both naturally-occurring substances such as protein, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds, for example, poly(vinylpyrrolidone), acrylamide polymers and the like. The vehicle or binder for the adduct can also comprise alone or in combination with hydrophilic water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described, for example, in Nottorf U.S. Pat. 3,142,568 issued July 28, 1964; White U.S. Pat. 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S. Pat. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911 issued Nov. 19, 1968.

The adduct can be added to the hydrophilic colloid by means well known in the art, for example, the adduct may be added from water solutions or suitable organic solvent solutions. The adducts can be added using various procedures including those described in Collins et al. U.S. Pat. 2,912,343 issued Nov. 10, 1959; McCrossen et al. U.S. Pat. 3,342,605 issued Sept. 19, 1967; Audran U.S. Pat. 2,996,287 issued Aug. 15, 1961 and Johnson et al. U.S. Pat. 3,425,835 issued Feb. 4, 1969.

The concentration of the adduct in the water permeable colloid can vary widely. The most desirable concentrations for a particular silver halide element can be determined by experimentation. The change in concentration will naturally affect the photographic speed. Suitable results appear to be obtained when the adduct is present at about .001 mg./ft.² to about 5 mg./ft.² of water permeable colloid. The preferred concentration is in a range of about .005 mg./ft.² to about .5 mg./ft.² of water permeable colloid.

In another embodiment of the invention the water permeable colloid coating compositions comprising the adducts as described hereinabove are utilized as an overcoat for a photographic element, especially a high-speed photo-

graphic element, for example, an X-ray photographic element or a color separation photographic film.

The coating comprising the water permeable colloid and the adduct may be coated according to various coating procedures well known in the art, for example, dip coating, air knife coating, curtain coating, or extrusion coating using hoppers of the type described in Belguin U.S. Pat. 2,681,294 issued June 15, 1954. When two or more layers are coated simultaneously procedures may be employed as described in Russell U.S. Pat. 2,761,791 issued Sept. 4, 1956 and Wynn British Pat. 837,095. This invention also can be used for silver halide layers coated by vacuum evaporation as described in British Pat. 968,453 and LuValle et al. U.S. Pat. 3,219,451 issued Nov. 23, 1965.

The coating composition comprising the water permeable colloid and the adduct may also contain any of the addenda normally utilized in photographic products.

The coating composition of this invention can contain other speed increasing compounds such as polyalkylene glycols, cationic surface active agents and thioethers or combinations of these as described in Piper U.S. Pat. 2,886,437 issued May 12, 1959; Dann et al. U.S. Pat. 3,046,134 issued July 24, 1962; Carrol et al. U.S. Pat. 2,944,900 issued July 12, 1960; and Goffe U.S. Pat. 3,294,540 issued Dec. 27, 1966.

The coating composition of this invention comprising the water permeable colloid and the adduct can contain antifoggants and stabilizers. Suitable antifoggants and stabilizers each used alone or in combination include thiazolium salts described in Brooker et al. U.S. Pat. 2,131,038 issued Sept. 27, 1938, and Allen et al. U.S. Pat. 2,694,716 issued Nov. 16, 1954; the azaindenes described in Piper U.S. Pat. 2,886,437 issued May 12, 1959, and Heimbach et al. U.S. Pat. 2,444,605 issued July 6, 1948; the mercury salts as described in Allen et al. U.S. Pat. 2,728,663 issued Dec. 27, 1955; the urazoles described in Anderson et al. U.S. Pat. 3,287,135 issued Nov. 22, 1966; the sulfocatechols described in Kennard et al. U.S. Pat. 3,236,652 issued Feb. 22, 1966; the oximes described in Carroll et al. British Pat. 623,448; nitron; nitroindazoles, the mercaptotetrazoles described in Kendall et al. U.S. Pat. 2,403,927 issued July 16, 1946; Kennard et al. U.S. Pat. 3,266,897 issued Aug. 16, 1966, and Luckey et al. U.S. Pat. 3,397,987 issued Aug. 20, 1968; the polyvalent metal salts described in Jones U.S. Pat. 2,839,405 issued Aug. 20, 1968; the thiuronium salts described in Herz et al. U.S. Pat. 3,220,839 issued Nov. 30, 1965; the palladium, platinum and gold salts described in Trivelli et al. U.S. Pat. 2,566,263 issued Aug. 28, 1951, and Yutzy et al. U.S. Pat. 2,597,915 issued May 27, 1952.

The coating composition of this invention comprising the water permeable colloid and the adduct may contain incorporated developing agents such as hydroquinones, catechols, aminophenols, 3-pyrazolidones, ascorbic acid and its derivatives, reductones and phenylendiamines. Combinations of developing agents can be employed in the practice of the invention. The developing agents can be in a silver halide emulsion and/or in another suitable location in the photographic element. The developing agents may be added from suitable solvents or in the form of dispersions as described in Yackel U.S. Pat. 2,592,368 issued Apr. 8, 1952, and Dunn et al. French Pat. 1,505,778.

The coating composition of this invention comprising the water permeable colloid and the adduct may contain plasticizers and lubricants such as polyalcohols e.g., glycerin and diols of the type described in Milton et al. U.S. Pat. 2,960,404 issued Nov. 1, 1966; fatty acids or esters such as those described in Robijns U.S. Pat. 2,588,765 issued Mar. 11, 1952, and Duane U.S. Pat. 3,121,060 issued Feb. 11, 1964, and silicone resins such as those described in Du Pont British Pat. 955,061.

The photographic layers employed in the practice of this invention may contain surfactants such as saponin;

anionic compounds such as the alkyl aryl sulfonates described in Baldsiefen U.S. Pat. 2,600,831 issued June 17, 1962; amphoteric compounds such as those described in Ben-Ezra U.S. Pat. 3,138,816 issued May 19, 1964; and water soluble adducts of glycidol and an alkyl phenol such as those described in Olin Mathieson British Pat. 1,022,878.

The various layers, including the photographic layers, employed in the practice of this invention can contain light absorbing materials and filter dyes such as those described in Sawday U.S. Pat. 3,253,921 issued May 31, 1966; Gaspar U.S. Pat. 2,274,782 issued Mar. 3, 1942; Silberstein et al. U.S. Pat. 2,527,583 issued Oct. 31, 1950, and Van Campen U.S. Pat. 2,956,879 issued Oct. 18, 1960. If desired, the dyes can be mordanted, for example, as described in Jones et al. U.S. Pat. 3,282,699 issued Nov. 1, 1966.

The addenda described hereinabove may also be incorporated in any of the other layers of a photographic element.

The overcoat of this invention can be located in a variety of physical positions with reference to the electromagnetic radiation sensitive silver salt layer. The overcoat can be the upper and outermost layer or any of the internal layers. Any layer contiguous to the silver halide layers can contain the adduct. The only limitation on the location of the adduct containing emulsion layer is that it should preferably not contain electromagnetic radiation sensitive silver halides since the adduct will tend to fog the silver and/or decrease the speed of the silver salt.

In another embodiment of this invention there is provided high-speed X-ray materials which can be developed in the presence of a hardening developer or a non-hardening developer. The X-ray materials comprise a support, at least one image recording layer such as a coarse-grained silver bromoiodide gelatin emulsion of the type employed in medical radiography, and the adduct containing hydrophilic colloid layer. The X-ray products normally contain a phosphor containing screen as an integral or separate part of element, said phosphors emitting in the ultraviolet region of the spectrum. The phosphors which may be employed in the X-ray elements of this invention are well known in the art. Phosphors which may be suitably employed in the X-ray products of this invention are disclosed, for example, in Belgium Pat. No. 703,998 of Luckey issued Mar. 18, 1968. Illustrative of the typical phosphors employed in radiography are, for example, lead activated barium sulfate, europium activated barium sulfate, europium activated barium strontium sulfate, lead sulfate and the like.

The novel coatings of this invention can be employed in combination with color sensitive material. In another embodiment, for example, there is provided photographic films for making color separations said film comprising a support, a coarsed-grained silver halide emulsion and an overcoat comprising the above described adducts. Typical photographic materials for making color separations are described in copending Sales in U.S. application Ser. No. 609,357 filed Jan. 16, 1967.

Processing of the photographic elements of this invention can be effected in a variety of ways including the multi-tank manual methods but preferably in a continuous machine processing system wherein the photographic element is processed by passing through rollers or otherwise in one continuous motion by transporting it into and out of at least one processing solution in the manner shown, for example, by U.S. Pats. 3,025,779 of Russell and Kunz issued Mar. 20, 1962; 3,078,024 of Sardeson issued Feb. 19, 1963; 3,122,086 of Fitch issued Feb. 25, 1964; 3,149,551 of Cramer issued Feb. 22, 1964; 3,156,173 of Meyer issued Nov. 10, 1964; and 3,224,356 of Fleisher and Hixon issued Feb. 21, 1965. A typical roller type

processing apparatus employed in the fast processing of X-ray materials is described in Belgian Pat. 700,301 issued Aug. 31, 1967, to Barnes et al.

The silver halide emulsions used with this invention can comprise silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide or mixtures thereof. The emulsions may be coarse or fine grain and can be prepared by any of the well-known procedures, e.g., single jet emulsions, double jet emulsions, such as Lippmann emulsions, ammoniacal emulsions, thiocyanate or thioether ripened emulsions such as those described in Nietz et al. U.S. Pat. 2,222,264 issued Nov. 4, 1940; Illingsworth U.S. Pat. 3,320,069 issued May 15, 1967; and McBride U.S. Pat. 3,271,157 issued Sept. 16, 1966. Surface image emulsions may be used or internal image emulsions such as those described in Davey et al. U.S. Pat. 2,592,250 issued Apr. 8, 1952; Porter et al. U.S. Pat. 3,206,313 issued Sept. 14, 1965; Berriman U.S. Pat. 3,367,778 issued Feb. 6, 1968, and Bacon et al. U.S. Pat. 3,447,927 issued June 3, 1969. If desired, mixtures of surfaces and internal image emulsions may be used as described in Luckey et al. U.S. Pat. 2,996,382 issued Apr. 15, 1961. Negative type emulsions may be used or direct positive emulsions such as those described in Leermakers U.S. Pat. 2,184,013 issued Dec. 19, 1939; Kendall et al. U.S. 2,541,472 issued Feb. 13, 1951; Berriman U.S. Pat. 3,367,778 issued Feb. 6, 1968; Schouwenaars British Pat. 723,019; Illingsworth et al. French Pat. 1,520,821; Ives U.S. Pat. 2,563,785 issued Aug. 7, 1951; Knott et al. U.S. Pat. 2,456,953 issued Dec. 21, 1968, and Land U.S. Pat. 2,861,885 issued Nov. 25, 1958. The emulsions may be regular grain emulsions such as the type described in Klein and Moisar, *J. Phot. Sci.*, vol. 12, No. 5, Sept./Oct. 1964, pp. 242-251.

The silver halide emulsions used with this invention may be unwashed or washed to remove soluble salts. In the latter case the soluble salts may be removed by chills setting and leaching or the emulsion may be coagulation washed, e.g., by the procedures described in Hewitson et al. U.S. Pat. 2,618,556 issued Nov. 18, 1972; Yutzy et al. U.S. Pat. 2,614,928 issued Oct. 21, 1952; Yackel U.S. Pat. 2,565,418 issued Aug. 21, 1951; Hart et al. U.S. Pat. 3,241,969 issued Mar. 22, 1966; and Waller et al. U.S. Pat. 2,489,341 issued Nov. 29, 1949.

The emulsions used with this invention may be sensitized with chemical sensitizers, such as with reducing agents; sulfur, selenium or tellurium compound; gold, platinum or palladium compounds; or combinations of these. Suitable procedures are described in Sheppard et al. U.S. Pat. 1,623,499 issued Apr. 5, 1927; Waller et al. U.S. Pat. 2,399,083 issued Apr. 23, 1946; McVeigh U.S. Pat. 3,297,447 issued Jan. 10, 1967; and Dunn U.S. Pat. 3,297,446 issued Jan. 10, 1967.

The photographic and other hardenable layers used in the practice of this invention can be hardened by various organic or inorganic hardeners, alone or in combination, such as the aldehydes, and blocked aldehydes, ketones, carboxylic and carbonic acid derivatives, sulfonate esters, sulfonyl halides and vinyl sulfonyl ethers, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides, mixed function hardeners and polymeric hardeners such as oxidized polysaccharides like dialdehyde starch and oxyguar gum and the like.

The photographic emulsions and elements described in the practice of this invention can contain various colloids alone or in combination as vehicles, binding agents and various layers. Suitable hydrophilic materials include both naturally-occurring substances such as proteins, for example, gelatin, gelatin derivatives, cellulose derivatives, polysaccharides such as dextran, gum arabic and the like; and synthetic polymeric substances such as water soluble polyvinyl compounds like poly(vinylpyrrolidone), acrylamide polymers and the like.

The described photographic emulsion layers and other layers of a photographic element employed in the practice

of this invention can also contain alone or in combination with hydrophilic, water permeable colloids, other synthetic polymeric compounds such as dispersed vinyl compounds such as in latex form and particularly those which increase the dimensional stability of the photographic materials. Suitable synthetic polymers include those described for example, in Nottorf U.S. Pat. 3,142,568 issued July 28, 1964; White U.S. Pat. 3,193,386 issued July 6, 1965; Houck et al. U.S. Pat. 3,062,674 issued Nov. 6, 1962; Houck et al. U.S. 3,220,844 issued Nov. 30, 1965; Ream et al. U.S. Pat. 3,287,289 issued Nov. 22, 1966; and Dykstra U.S. Pat. 3,411,911 issued Nov. 19, 1968; particularly effective are those water-insoluble polymers of alkyl acrylates and methacrylates; acrylic acid, sulfoalkyl acrylates or methacrylates, those which have cross-linking sites which facilitate hardening or curing, and those having recurring sulfobetaine units as described in Dykstra Canadian Pat. 774,054.

The photographic elements used with this invention may contain antistatic or conducting layers, such layers may comprise soluble salts, e.g., chlorides, nitrates, etc., evaporated metal layers, ionic polymers such as those described in Minsk U.S. Pat. 2,861,056 issued Nov. 18, 1958, and Sterman et al. U.S. Pat. 3,206,312 issued Sept. 14, 1965 or insoluble inorganic salts such as those described in Trevo U.S. Pat. 3,428,451 issued Feb. 18, 1969.

The photographic layers and other layers of a photographic element employed and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically, a flexible support is employed, especially a paper support, which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer, particularly a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylenebutene copolymers and the like.

The photographic elements used in this invention may contain brightening agents including stilbenes, triazines, oxazoles and coumarin brightening agents. Water soluble brightening agents may be used such as those described in Albers et al. German Pat. 972,067 and McFall et al. U.S. Pat. 2,933,390 issued Apr. 19, 1960, or dispersions of brighteners may be used such as those described in Jansen German Pat. 1,150,274, Oetiker et al. U.S. Pat. 3,406,070 issued Oct. 15, 1968, and Heidke French Pat. 1,530,244.

Spectral sensitizing dyes can be used conveniently to confer additional sensitivity to the light sensitive silver halide emulsion of the multilayer photographic elements of the invention. For instance, additional spectral sensitization can be obtained by treating the emulsion with a solution of a sensitizing dye in an organic solvent or the dye may be added in the form of a dispersion in Owens et al. British Pat. 1,154,781. For optimum results, the dye may either be added to the emulsion as a final step or at some earlier stage.

Sensitizing dyes useful in sensitizing such emulsions are described, for example, in Brooker et al. U.S. Pat. 2,526,632 issued Oct. 24, 1950; Sprague U.S. Pat. 2,503,776 issued Apr. 11, 1950; Brooker et al. U.S. Pat. 2,493,748 issued Jan. 10, 1950; and Taber et al. U.S. Pat. 3,384,486 issued May 21, 1968. Spectral sensitizers which can be used include the cyanines, merocyanines, complex (tri or tetranuclear) merocyanines, complex (tri or tetranuclear) cyanines, holopolar cyanines, styryls, hemicyanines (e.g. enamine hemicyanines), oxonols and hemioxonols.

Dyes of the cyanine classes may contain such basic nuclei as the thiazolines, oxazolines, pyrrolines, pyridines, oxazoles, thiazoles, selenazoles and imidazoles. Such nuclei may contain alkyl, alkylene hydroxyalkyl, sulfoalkyl, carboxyalkyl, aminoalkyl and enamine groups and may be fused to carbocyclic or heterocyclic ring systems either unsubstituted or substituted with halogen, phenyl,

alkyl, haloalkyl, cyano, or alkoxy groups. The dyes may be symmetrical or unsymmetrical and may contain alkyl, phenyl, enamino or heterocyclic substituents on the methine or polymethine chain.

The merocyanine dyes may contain the basic nuclei mentioned above as well as acid nuclei such as thiohydantoin rhodanines, oxazolinediones, thiazolidenediones, barbituric acids, thiazolineones, and malononitrile. These acid nuclei may be substituted with alkyl, alkylene, phenyl, carboxyalkyl, sulfoalkyl, hydroxyalkyl, alkoxyalkyl, akyamino groups, or heterocyclic nuclei. Combinations of these dyes may be used, if desired. In addition, supersensitizing addenda which do not absorb visible light may be included, for example, ascorbic acid derivatives, azaindenes, cadmium salts, and organic sulfonic acids as described in McFall et al. U.S. Pat. 2,933,390 issued Apr. 19, 1960 and Jones et al. U.S. Pat. 2,937,089 issued May 17, 1960.

This invention may be used with elements designed for colloid transfer processes such as described in Yutzky et al. U.S. Pat. 2,716,059 issued Aug. 23, 1955; silver salt diffusion transfer processes such as described in Rott U.S. Pat. 2,352,014 issued June 20, 1944, Land U.S. Pat. 2,543,181 issued Feb. 27, 1951, Yackel et al. U.S. Pat. 3,020,155 issued Feb. 6, 1962, and Land U.S. Pat. 2,861,885 issued Nov. 25, 1958; color image transfer processes such as described in Rogers U.S. Pat. 3,087,817 issued Apr. 30, 1963; 3,185,567 issued May 25, 1965; and 2,983,606 issued May 9, 1961; Weyerts et al. U.S. Pat. 3,253,915 issued May 31, 1966; Whitmore et al. U.S. Pat. 3,227,550 issued Jan. 4, 1966; Barr et al. U.S. Pat. 3,227,551 issued Jan. 4, 1966; Whitmore U.S. Pat. 3,227,552 issued Jan. 4, 1966; and Land U.S. Pat. 3,415,644 issued Dec. 10, 1968; 3,415,645 issued Dec. 10, 1968; 3,415,646

issued Sept. 18, 1956; to provide a relief image as described in Woodward U.S. Pat. 3,402,045 issued Sept. 17, 1968, or Spencer U.S. Pat. 3,053,658 issued Sept. 11, 1962; to prepare a relief printing plate as described in Baxter et al. U.S. Pat. 3,271,150 issued Sept. 6, 1966.

This invention can be further illustrated by the following examples of preferred embodiments thereof, although it will be understood that these examples are included merely for illustrating this invention.

EXAMPLE 1-7

A coarse-grained silver bromoiodide gelatin photographic emulsion of the type used in medical X-ray films is coated on a poly(ethyleneterephthalate) film support at a coverage of 435 mg. of silver/ft.² and 288 mg. of gelatin/ft.². Over the emulsion layer is coated a gelatin layer at a coverage of 130 mg. of gelatin/ft.² containing the ingredients listed in Table I. The samples are exposed on an intensity scale sensitometer and processed in an automatic processing machine of the type described in U.S. Pat. 3,147,090 using a hardening developer of the type described in U.S. Pat. 3,232,761 with a total processing time of 90 seconds.

In Example 4-7, an adduct of L-cysteine and glutaraldehyde is prepared by combining desired ratios of the two compounds in an aqueous solution at a pH of 5.6 and holding the mixture for 24 hours before addition to gelatin solutions.

The results as summarized in Table I illustrate that an adduct as described herein, when incorporated in a photographic element increases the speed of the element as compared to those elements containing either cysteine or glutaraldehyde alone, or an element which contains neither glutaraldehyde or cysteine.

TABLE I
(Processed in Hardening Developer)

Example	Addenda ¹	Molar ratio ²	Mg./ft. ²	Fresh test			1 wk. incubations		
				Rel. speed	γ	D _{min.}	Rel. speed	γ	D _{min.}
1	-----	-----	100	3.65	.01	120	2.73	.02	
2	B	-----	(.157)	138	3.38	.02	135	2.63	.02
3	A	-----	(.274)	145	3.56	.03	115	3.02	.17
4	C	1:1	{ A (.1028) B (.0600) }	178	3.40	.01	174	2.74	.07
5	C	1:2	{ A (.0685) B (.0785) }	166	3.45	.02	174	2.75	.06
6	C	1:4	{ A (.0410) B (.0943) }	155	3.46	.02	166	2.73	.02
7	C	1:4	{ A (.0820) B (.1886) }	178	3.40	.02	182	2.54	.08

¹ A=L-cysteine; B=Glutaraldehyde; C=Adduct of L-cysteine and glutaraldehyde.
² Compound A to Compound B.

issued Dec. 10, 1968; and imbibition transfer processes as described in Minsk U.S. Pat. 2,882,156 issued Apr. 14, 1959.

This invention may be used with elements designed for color photography, for example, elements containing color-forming couplers such as those described in Frohlich et al. U.S. Pat. 2,376,679 issued May 22, 1945, Jelley et al. U.S. Pat. 2,322,027 issued June 15, 1943; Fierke et al. U.S. Pat. 2,801,171 issued July 30, 1957, Godowsky U.S. Pat. 2,698,794 issued Jan. 4, 1966, Barr et al. U.S. Pat. 3,227,554 issued Jan. 4, 1966, and Graham et al. U.S. Pat. 3,046,129 issued July 24, 1962; or elements to be developed in solutions containing color-forming couplers such as those described in Mannes et al. U.S. Pat. 2,252,718 issued Aug. 19, 1941, Carroll et al. U.S. Pat. 2,592,243 issued Apr. 8, 1952, and Schwan et al. U.S. Pat. 2,950,970 issued Aug. 30, 1960; and in false-sensitized color materials such as those described in Hanson U.S. Pat. 2,763,549 issued Sept. 18, 1956.

The silver halide emulsions used with this invention can be used for making lithographic printing plates such as by the colloid transfer of undeveloped and unhardened areas of an exposed and developed emulsion to a suitable support as described in Clark et al. U.S. Pat. 2,763,533

EXAMPLES 8-12

Examples of the photographic elements prepared in the same manner as in Examples 1-7 are processed for 6 minutes in a conventional Elon-hydroquinone developer containing no hardening agent, fixed and washed. The results are summarized in Table II.

TABLE II
(Processed in Non-Hardening Developer)

Example	Addenda ¹	Molar ratio of A to	Mg./ft. ²	Rel. speed	γ	D _{min.}
8	-----	-----	80	2.79	.02	
9	B	-----	(.157)	110	2.75	.02
10	A	-----	(.274)	115	2.77	.02
11	C	1:4	{ A (.0410) B (.0943) }	148	2.60	.04
12	C	1:4	{ A (.0820) B (.1886) }	282	2.12	.13

¹ A=L-cysteine; B=Glutaraldehyde; C=Adduct of L-cysteine and glutaraldehyde.

Similar results are obtained when other hydrophilic colloid vehicles other than gelatin are partially substituted for gelatin, for example, the overcoat layer can contain a mixture of gelatin and hydrophilic colloids such as disclosed in Belgian Pat. 731,212.

11 EXAMPLE 13

The following example illustrates the adducts employed in this invention increase the speed of other high speed negative materials.

A color separation photographic film, identified as Film A in Table III, is prepared in the manner as described in Salesin Belgian Pat. 709,397 issued Feb. 15, 1968, containing the described green-light absorbing dye, is coated on a polyethylene terephthalate support at 775 mg. of silver/ft.² and 850 mg. of gelatin/ft.².

The emulsion layer is overcoated with a gelatin layer at 82 mg./ft.².

A film, identified as B in Table III, is prepared in the manner of the above film except to the gelatin overcoat layer is added the adduct of L-cysteine (0.045 mg./ft.²) and glutaraldehyde (0.105 mg./ft.²).

Both of the above coatings are exposed on an Eastman

12 EXAMPLES 19-22

Samples of a coarse-grained silver bromiodide gelatin emulsion of the type used in medical X-ray films are coated on a poly(ethylene terephthalate) film support at a coverage of 435 mg. of silver/ft.² and 288 mg. of gelatin/ft.². Samples of the emulsion layers are coated with a gelatin layer at a coverage of 130 mg. of gelatin/ft.² containing a preformed adduct of L-cysteine and acrylic aldehyde. The samples are exposed on an intensity sensitometer and processed in an automatic processing machine of the type described in U.S. Pat. 3,147,090 using either a hardening or non-hardening developer.

The adduct is prepared by combining, at a ratio of 1:4, L-cysteine and acrylic aldehyde in an aqueous solution at a pH of 5.6 and aging the mixture for 24 hours before addition to gelatin solutions.

The results are summarized in Table V.

TABLE V

Example	Addenda ¹	Molar ratio ²	Mg./ft. ²	Fresh test			1 wk. incubation		
				Rel. speed	γ	D _{min.}	Rel. speed	S	D _{min.}
Processed in hardening developer:									
19.....				100	3.21	.01	112	3.04	.02
20.....	E	1:4	{ A (.0366) D (.0457) }	118	3.32	.01	178	2.93	.04
Processed in non-hardening developer:									
21.....				83	2.76	.01	100	2.63	.02
22.....	E	1:4	{ A (.0366) D (.0457) }	97	2.71	.01	166	2.45	.04

¹ A=L-cysteine; D=Acrylic aldehyde; E=Adduct of A and D.

² Compound A to Compound D.

1 B Sensitometer $\frac{1}{8}$ " to a 500 watt bulb modulated by Kodak Wratten Filter No. 29 (red), No. 61+16 (green) and No. 35+38A (blue) and processed for 5 minutes.

The developed separation films are washed, fixed in a conventional alkali metal thiosulfate fixing bath, washed and dried. Sensitometric measurements are made of each of the separation images with the results summarized in Table III.

TABLE III

Filter	Film	Relative speed	Contrast	Fog
Blue.....	A	100	1.82	.03
Do.....	B	135	1.70	.05
Green.....	A	100	1.85	.03
Do.....	B	126	1.67	.05
Red.....	A	100	2.00	.03
Red.....	B	135	1.84	.05

EXAMPLES 14-18

The following examples illustrate the particularity of the adduct with reference to the emulsion layer wherein said adduct is employed.

Samples of photographic elements prepared in the manner as in Examples 1-7 except that the adduct is added to the silver halide layer. The results are summarized in Table IV.

TABLE IV

Ex. No.	Addenda ¹	Mg./ft. ²	Fresh test		1 wk. incubation	
			Relative speed	D _{min.}	Relative speed	D _{min.}
14....	(Control)		100	.04	91	.06
15....	Adduct.....	{ A (.56) B (1.3) }	8.3	2.17	-----	2.39
16....	do.....	{ A (.28) B (.65) }	105	1.13	91	.97
17....	do.....	{ A (.0672) B (.156) }	112	.13	100	.15
18....	do.....	{ A (.0336) B (.078) }	102	.06	95	.08

¹ A=L-cysteine; B=Glutaraldehyde.

The above table illustrates that the advantages obtained through incorporating the adduct in an overcoat are lost when the adduct is added to the silver halide emulsion. The table illustrates that when the adduct is added at a high level, excessive fog results and when the adduct is added at lower levels, no speed advantage is obtained.

EXAMPLES 23-26

Samples of an X-ray material are prepared as in Examples 19-22 except, as specified in Table VI, a dispersion of a high boiling substantially water insoluble organic liquid of the type described in Jelley et al. U.S. Pat. 2,322,027 and Vittum et al. U.S. Pat. 2,801,170, e.g., tricresyl phosphate is added to the silver halide emulsion layer. The samples are processed as described above. The results are summarized in Table VI below.

TABLE VI

Example	Adduct ¹ (mg./ft. ²)	Organic liquid (g./ft. ²)	Fresh		
			Rel. speed	γ	Fog
23.....			100	3.10	.06
24.....	{ A (.016) B (.035) }		141	2.93	.06
25.....		.14	145	3.15	.06
26.....	{ A (.016) B (.035) }	.14	229	2.76	.08

¹ A=L-cysteine; B=Glutaraldehyde.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

There is claimed:

1. In a photographic element comprising a support bearing at least one electromagnetic radiation-sensitive silver halide layer, the improvement being wherein said element contains on the same side of the support as said layer, a distinct layer comprising an adduct of a first compound which is cysteine, DL-penicillamine, DL-homocysteine-thiolactone or 2-aminoethanethiol with a second compound which is glutaraldehyde or acrylic aldehyde.

2. A photographic element of claim 1 wherein said first compound is cysteine.

3. A photographic element of claim 1 wherein said second compound is glutaraldehyde.

4. A photographic element of claim 1 wherein said distinct layer comprises gelatin.

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5. A photographic element of claim 1 wherein said adduct is present at about 0.001 mg./ft.² to about 5 mg./ft.² of gelatin.

6. A photographic element of claim 1 wherein said preformed adduct comprises from about 1 to about 8 mole equivalents of said second compound to about 1 mole equivalent of said first compound.

7. A photographic element of claim 1 wherein said radiation-sensitive silver halide layer comprises a coarse-grained silver bromiodide emulsion.

8. A photographic element of claim 7 wherein said silver bromide layer comprises a black-and-white panchromatically sensitized silver bromiodide emulsion.

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References Cited

UNITED STATES PATENTS

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NORMAN G. TORCHIN, Primary Examiner

W. H. LOUIE, Jr., Assistant Examiner

U.S. Cl. X.R.

106—125

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,708,302 Dated January 2, 1972

Inventor(s) James Plakunov and James E. Koller

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Claims:

Column 13, line 14, after claim 8, should be inserte

--- 9. A photographic element of Claim 1 wherein said distinct layer is contiguous to said silver halide layer.

10. In a black-and-white photographic element adapted for color separation materials comprising a support, a silver halide emulsion and a layer distinct from the silver halide emulsion, the improvement wherein said layer comprises L-cysteine-glutaraldehyde adduct.

11. In a radiographic element comprising a support bearing at least one image recording layer and a layer distinct from said image recording layer, the improvement wherein said distinct layer contains a L-cysteine-glutaraldehyde adduct.---

Column 1, line 10, "8 Claims" should read
-- 11 Claims --.

Signed and sealed this 26th day of February 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents