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(54) Photographic element with improved scratch resistance

(57) A photographic element having improved scratch resistance and abrasion resistance is disclosed. The imaging element includes a support, at least one light-sensitive layer, and a protective layer. The protective layer has a UV ray absorbing dye layer which includes a UV ray absorbing dye, a high boiling point organic solvent and a hydrophilic binder. The protective layer has an outermost layer which includes a matting agent and a modified gelatin having at least one carboyxlic acid moiety where at least one carboxylic acid moiety of gelatin is modified into a monoamide of a polyamine whereby at least one additional amine group is introduced.

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Description

FIELD OF THE INVENTION:

This invention relates to an imaging element, and in particular to a silver halide photographic element with improved scratch and abrasion resistance.

BACKGROUND OF THE INVENTION

It is conventional to incorporate an absorbing dye, in particular, an ultraviolet ray absorbing dye, into a light-insensitive layer in a photographic element to absorb light in a specific wavelength region. The dyed light-insensitive layer is used, for example, to control the spectral composition of light incident upon a photographic emulsion layer, to act as an antihalation layer between the support and the photographic emulsion layer, or on the side of the support opposite to the photographic emulsion layer to prevent halation caused by light scattering during and after the passage of light through the photographic emulsion layer, or to absorb or to remove ultraviolet light produced by static discharge generated by friction of separation, which occurs when the surfaces of the photographic element come into contact during production or treatment processes. When accumulation of static electricity by charging reaches a certain limiting value, atmospheric discharge occurs at a particular moment and a discharge spark fires at the same time. When the photographic element is exposed to light by discharging, static marks appear after development.

Different methods for incorporating absorbing dyes into a non-imaging layer have been described in for example, US Patent Nos. 2,739,888, 3,352,681, and 3,7077,375, where an oil soluble dye is dissolved in a high boiling organic solvent, and mixed under high shear or turbulence together with an aqueous medium, which may also contain a surfactant, in order to break the organic phase into submicron particles dispersed in the continuous aqueous phase. However, when such dye dispersions are used in a light-insensitive layer, the layer becomes soft and the mechanical properties of the layer are lowered. Furthermore, even if no high boiling solvent is used, many dyes themselves are liquid, and they therefore can have a detrimental effect on the mechanical properties of the layer and adhesion with an adjacent layer.

The weakening of light-insensitive layers by an absorbing dye dispersion, in particular by an ultraviolet absorbing dye dispersion, has been a serious problem in, for example, color light sensitive materials, where a light-insensitive layer containing an ultraviolet dye dispersion is often coated as a protective layer on the top of the emulsion layer to remove the ultraviolet light generated by static discharge and for correct color reproduction. Since it is desired to record only visible light, the influence of the ultraviolet light is very apparent. For example, when photographing objects which have a comparatively large quantity of spectral energy in the ultraviolet region, such as a distant view, a snow scene, or an asphalted road, etc. the resulting color images are rich in blue color. Accordingly, in order to obtain color photographic images which have correct color reproduction, it is desired to prevent ultraviolet rays from reaching the silver halide emulsion layers. Very often, another light-insensitive layer containing a matting agent is coated as the outermost protective layer above the light-insensitive layer containing the ultraviolet absorbing dye dispersions for better resistance to ferrotyping and sticking at high temperature and in moist environments. Photographic materials with such layer structures often show inferior physical and mechanical properties during various handling processes, such as coating, drying, finishing, winding, rewinding, printing, and so on. For example, scratches and abrasion marks are easily generated on photographic material front and back surfaces by contact friction with other apparatus or photographic surfaces. The generated scratches and abrasion marks can deface the image during printing and projection processes. On irreplaceable negatives, the physical scratches may require very expensive retouching.

Various methods have been proposed to obtain a physically improved photographic material by reducing the contact friction of the photographic material to other surfaces so that it will not be damaged during the manufacturing, exposure, developing and printing or projecting processes. For example, methods for reducing the contact friction were described: in US Patent No. 3,042,522 by incorporating both a silicone fluid and a certain surface active agent into the protective overcoat; in US Patent No. 3,080,317 by using a mixture of dimethyl silicone and diphenyl silicone on the backside of the support; in GB Patent No. 1,143,118 by incorporating a triphenyl terminated methyl phenyl silicone into the emulsion protective overcoat; in US Patent No. 3,489,567 by using a combination of dimethyl silicone and beta-alanine derived surfactants; in US Patent No. 3,121,060 by using modified sperm oils in the protective overcoat; in US Patent No. 4,004,927 by using liquid organopolysiloxane with methyl and alkyl ($>C_1$) or aryl, or aralkyl side groups in the protective overcoat, and in US Patent No. 4,4047,958 by using polysiloxane with polyether side chains on the backside of the support.

Various methods have also been proposed to reinforce the surface overcoat layer, for example, in GB Patent No. 1,270,578 by adding a certain class of hardener to gelatin; in US Patent No. 3,053,662 by using colloidal silica in the overcoat layer; in US Patent No. 4,268,623 by using colloidal silica in combination with a water soluble polymer having a carboxylic acid group in the overcoat layer; in US Patent No. 4,777,113 by using two overcoat layers, the upper layer containing a colloidal silica and the lower layer containing a polymer latex; and in US Patent No. 4,914,012 by using a composite latex comprising a polymeric acrylic acid ester and/or a polymeric methacrylate acid ester and colloidal silica. However, the use of colloidal silica particles in the surface protective layer suffers from a number of disadvantages, for example: they increase significantly the coating solution viscosities; they increase the brittleness of the protective layer; they adhere to wall surfaces and therefore give rise to extensive cleaning of equipment and increased labor cost; and they are highly abrasive and therefore may increase the wear of manufacturing and processing equipment.

In recent years, the conditions under which the photographic materials are manufactured or utilized have become even more severe, either because their applications have been extended, for example, in an atmosphere of high humidity and high temperature, or because the methods for their preparation have been advanced, for example, the use of high speed coatings, high speed finishing and cutting, and fast processing, or because their emulsion layers have been progressively thinned. Under these conditions, the aforementioned photographic materials are more severely scratched, and they have been subjected to a high level of customer comments and complaints from the scratched negatives and printable scratches on the prints.

Therefore, a foremost objective of the present invention is to provide a silver halide photographic material which exhibits excellent resistance to such physical scratches and abrasions.

SUMMARY OF THE INVENTION

In accordance with the present invention, a photographic element comprises a support, at least one light-sensitive layer, and a light-insensitive protective layer. The light-insensitive protective layer includes at least two layers, with the layer closer to the support (UV layer) containing at least one ultraviolet ray absorbing dye, a high boiling organic solvent, and a hydrophilic binder, and with the layer farthest from the support (outermost protective layer) containing a processing surviving matting agent and a modified gelatin where at least one carboxylic acid moiety of gelatin is modified into a monoamide of a polyamine whereby at least one additional amine group is introduced.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described in detail.

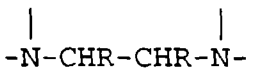
The photographic element of the present invention has a light-insensitive hydrophilic protective layer which includes at least two layers. The layer closer to the support contains at least one ultraviolet absorbing dye, a high boiling organic solvent, and a hydrophilic binder. The layer farthest from the support contains at least one matting agent and a modified gelatin.

The content of the hydrophilic binder in the UV layer is defined as the ratio of coating weight of the hydrophilic binder to the sum of the coating weights of the ultraviolet absorbing dyes, high boiling organic solvents, the hydrophilic binder, and other addenda, and is preferably in the range of from 30 to 90%, and more preferably from 40 to 80%. The matte particle in the outermost layer has a mean particle size of from 0.5 to 10 μm, preferably from 1 to 5 μm, and most preferably from 1 to 3 μm, and a coating weight of from 0.01 g/m^2 to 0.3 g/m^2, preferably from 0.02 g/m^2 to 0.2 g/m^2, and most preferably from 0.03 to 0.15 g/m^2.

The thickness of the UV layer of the present invention is usually 0.2 to 3 μm, and preferably from 0.5 to 2 μm. The thickness of the outermost protective layer is usually 0.4 to 3 μm, and more preferably 0.6 to 2 μm. The total thickness of the two layers is 0.6 to 6 μm, and preferably 1.5 to 4 μm. The term of "thickness" used herein refers to the thickness of the portion in which no matting agents are present, and measured from, for example, an electron micrograph of a non-swollen cross-section of the light-sensitive material.

The modified gelatin for use in accordance with the present invention has some of its free carboxyl groups converted into a monoamide of a polyamine thereby introducing at least one additional amine group. A preferred method of providing such a modified gelatin has been described in detail in U.S. Patent No. 5,219,992.

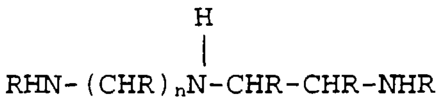
The polyamine mentioned above has the characteristic group:



$$\overset{|}{-N}-CHR-CHR-\overset{|}{N}-$$

Preferably each R is hydrogen, but each R may be an alkyl group as defined below. As indicated by the formula, the polyamine is a diamine, or a derivative thereof.

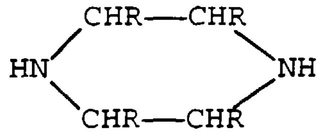
In the polyamine, at least two amine nitrogens must be separated by a two carbon bridge. In triamines, it is preferred that all three amino nitrogens be separated by two carbons. Polyamines of this type may be acyclic or cyclic. Acyclic diamines of this type are illustrated by ethylenediamine, 1,2-diaminopropane, N-methylethylenediamine and N,N'-dimethylethylenediamine. Diethylenetriamine is another illustrative amine that can be employed. It illustrates the use of triamines such as



$$RHN\text{-}(CHR)_nN(H)\text{-}CHR\text{-}CHR\text{-}NHR$$

wherein R and n are as defined below.

The polyamine with the characteristic group need not be acyclic, thus, for example, the polyamine may be cyclic, as in piperazine or piperazine derivatives:



In such compounds, each R is preferably hydrogen; hence, piperazine is a preferred cyclic amine for use in this invention. One of the hydrogens in the piperazine nucleus may be substituted with a HNR-CHR-CHR- group. Thus, another preferred polyamine is N-(2-aminoethyl)piperazine. Other cyclic diamines having at least one pair of ring nitrogens separated by a -CHR-CHR- bridge can be employed. The nitrogens may also be connected by a bridge of one to four carbons.

Preferred polyamines have 2 to 12 carbon atoms; more preferably 2 to 8 carbons. Preferably, the polyamines can be added to the reaction mixture as a salt; more preferably a hydrohalide salt derived from HCl or HBr. Thus, for example, ethylenediamine can be added to the reaction mixture as the dihydrochloride,

$$HCl.NH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2.HCl$$

The term "gelatin" used herein for the starting material for preparing the modified gelatin according to the invention relates to the protein substance emanating from collagen. However, this term is also intended to encompass other substantially equivalent substances, for example synthetic gelatin. In general, gelatin is classified as alkaline gelatin which is obtained from collagen, for example by treatment with calcium hydroxide; acidic gelatin which is obtained by acidic treatment, for example with hydrochloric acid; enzymatic gelatin which is treated, for example, with a hydrolase and low molecular weight gelatin which is obtained by further hydrolysis of the gelatins mentioned above by different methods. Each of the gelatins mentioned above may be used for the preparation of the modified gelatin required in accordance with the invention.

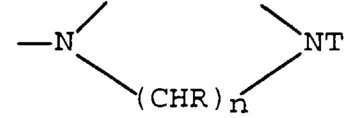
For one of the preferred embodiments, the modified gelatin has the formula:

$$Gel—CO—G$$

wherein Gel is a gelatin polypeptide, -CO- is a carbonyl group from a free carboxyl group in an aspartic acid or a glutamic acid moiety in said polypeptide, and G is

$$—NR—CHR—CHR—NR—T$$

or



wherein each R is independently hydrogen or a primary or secondary alkyl group of one to four carbon atoms, n is a positive integer having a value of one to four, and T is hydrogen or

$$CH_2—CH_2—NR—H;$$

said modified gelatin being further characterized by having from 1% to 40% of the free carboxyl groups in aspartic or glutamic acid moeities in said polypeptide being substitued with G-groups.

The types of ultraviolet ray absorbers (UV dyes) used in the present invention are not particularly limited provided their absorption maximum wavelengths fall within the range from 300 to 400 nm, and they have no harmful effect on the photographic properties of the element. Such UV dyes include ultraviolet absorbers of the thiazolidone type, the benzotriazole type, the cinnamic acid ester type, the benzophenone type, and the aminobutadiene type and have been described in detail in, for example, US patent Nos. 1.023,859, 2,685,512, 2,739,888, 2,748,021, 3,004,896, 3,052,636, 3,215,530, 3,253,921, 3,533,794, 3,692,525, 3,705,805, 3,707,375, 3,738,837, 3,754,919, and British Patent No 1,321,355.

The amount of UV absorbers used in the present invention is in the range of from 0.05 to 1 g/m^2, and preferably 0.1 to 0.5 g/m^2. The aforementioned UV absorbers are so selected as to have an absorption maximum in a wavelength region required for the photographic performance, and are used singly or in combination.

The UV dyes used for the present invention are preferably used in a pre-dispersion form (UV dye dispersion), which can be prepared, for example by dissolving the UV dye in a high boiling organic solvent and then adding the resulting solution in an aqueous gelatin solution containing a surfactant such as, for example, sodium dodecyl sulfonate. The mixture is stirred at high speed to make an emulsified dispersion, and the dispersion is added to the coating liquid, which is then coated. Those UV absorbers which are liquid at room temperature can be emulsified and dispersed without the use of high boiling organic solvent, and are preferable in the present invention. Typical high boiling organic solvents useful for the present invention have a boiling point of 175 °C or more at atmospheric pressure, and include, for example, phthalic esters, e.g. dibutyl phthalate, dipentyl phthalate, didodecyl phthalate, didecyl phthalate, diethylhexyl phthalate, dicyclohexyl phthalate, phosphanate or phosphanate esters, e.g. tricresyl phosphate, trihexyl phosphate, tri(2-ethyl hexyl) phosphate, tridodecyl phosphate, benzoate esters, e.g. 2-ethylhexyl benzoate, dodecyl benzoate, 2-ethylhexyl-*p*-hydroxybenzoate, alcohols and phenols, e.g. *p*-dodecyl phenol isostearyl alcohol, 2,4-tert-amylphenol, aliphatic carboxylate esters, an aniline derivative, and hydrocarbons. High boiling organic solvents which can be used for the practice of the present invention are described further in detail in, for example, US Patent No. 2,322,027, WO 94/11787.

Various matting agents can be used in the present invention. Such particles include, for example, inorganic particles such as silicon dioxide, barium sulfate, desensitized silver halide, zinc particles, calcium carbonate, and the like. In many cases, organic particles may be preferred. Organic matte particles can be made of cellulose esters, cellulose ethers, starches, addition-type polymers and interpolymers prepared from ethylenically unsaturated monomers such as acrylates including acrylic acid, methacrylates including methacrylic acid, acrylamides and methacrylate amides, itaconic acid and its half esters and diesters, styrenes including substituted styrenes, acrylonitriles and methcrylonitriles, vinyl acetates, vinyl ethers, vinyl and vinylidene halides and olefins. The matte particles can be crosslinked. In such cases, crosslinking monomers such as 1,4-butyleneglycol methacrylate, trimethylolpropane triacetate, allyl methacrylate, diallyl phthalate, divinyl benzene, and the like may be used. Other polymers that may comprise matting particles include condensation polymers such as polyurethanes, polyesters, polyamides, epoxies, and the like. Matte particles useful for the present invention are described in further detail in Research Disclosure No. 308, published Dec. 1989, pages 1008 to 1009.

When the matte particles are polymeric in nature, they may include reactive functional groups which form covalent bonds with binders by intermolecular crosslinking or by reaction with a crosslinking agent (i. e. a hardener). Suitable reactive functional groups include: hydroxyl, carboxyl, carbodiimide, epoxide, aziridine, vinyl sulfone, sulfinic acid, active methylene, amino, amide, allyl, and the like. There is no particular restriction on the amount of reactive groups present, but their concentrations are preferably in the range of from 0.5 to 10 weight percent. The particle surface may be surrounded with a layer of colloidal inorganic particles as described in US Patent No. 5,288,598, or a layer of colloidal polymer latex particles which have affinity with a suitable binder as described in US Patent No. 5,279,934, or a layer of gelatin as described in US Patent No. 4,855,219.

Processing removable mattes can be used together with a processing survival matte particle in the practice of the invention to further enhance the resistance of the photographic element to ferrotyping and blocking. Such processing removable matte include particles of, for example; copolymers of alkyl (meth)acrylates and methacrylic acid, or acrylic acid, or itaconic acid, copolymers of alkyl (meth)acrylates and maleic monoesters or monoamides, copolymers of styrene or vinyl toluene and a,b-unsaturated mono- or di-carboxylic acids, or dicarboxylic monoesters or monoamides, graft copolymers containing maleic anhydride or methacrylic acid, and dicarboxylic acid mono-ester of a cellulose derivative, such as phthalate and hexahydro phthalate of methyl cellulose, hydroxyethyl cellulose, or hydroxypropylomethyl cellulose. Such processing soluble mattes are described in further detail in US Patent No 2.992,101; 3,767,448;

4,094,848; 4,447,525; and 4,524,131.

Any suitable hydrophilic binder can be used in the UV layer in practice of the present invention. Gelatin is the most preferred hydrophilic binder. Other hydrophilic binders include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives (e.g. cellulose esters), polysaccharides, casein, and the like, and synthetic water permeable colloids such as poly(vinyl lactams), acrylamide polymers, poly(vinyl alcohol) and its derivatives, hydrolyzed polyvinyl acetates, polymers of alkyl and sulfoalkyl acrylates and methacrylates, polyamides, polyvinyl pyridine, acrylic acid polymers, maleic anhydride copolymers, polyalkylene oxide, methacrylamide copolymers, polyvinyl oxazolidinones, maleic acid copolymers, vinyl amine copolymers, methacrylic acid copolymers, acryloyloxyalkyl sulfonic acid copolymers, vinyl imidazole copolymers, vinyl sulfide copolymers, homopolymer or copolymers containing styrene sulfonic acid, and the like. For a crosslinkable binder such as gelatin, the binder is preferably crosslinked so as to provide a high degree of cohesion and adhesion. Crosslinking agents or hardeners which may effectively be used in the coating compositions of the present invention include aldehydes, epoxy compounds, polyfunctional aziridines, vinyl sulfones, methoxyalkyl melamines, triazines, polyisocyanates, dioxane derivatives such as dihydroxydioxane, carbodiimides, chrome alum, zirconium sulfate, and the like.

Any lubricant can be used in the outermost layer of the present invasion. Typical lubricants include (1) silicone based materials disclosed, for example, in US Patent Nos. 3,489,567; 3,080,317; 3,042,522; 4,004,927; and 4,047,958; and in British Patent Nos. 955,061 and 1,143,118; (2) higher fatty acids and derivatives, higher alcohols and derivatives, metal salts of higher fatty acids, higher fatty acid esters, higher fatty acid amides, polyhydric alcohol esters of higher fatty acids, etc disclosed in US Patent Nos. 2,454,043; 2,732,305; 2,976,148; 3,206,311; 3,933,516; 2,588,765; 3,121,060; 3,502,473; 3,042,222; and 4,427,964; in British Patent Nos. 1,263,722, 1,198,387; 1,430,997, 1,466,304, 1,320,757, 1,320,565, and 1,320,756, and in German Patent Nos. 1,284,295 and 1,284,294; (3) liquid paraffin and paraffin or wax like materials such as carnauba wax, natural and synthetic waxes, petroleum waxes, mineral waxes and the like; (4) perfluoro- or fluoro- or fluorochloro-containing materials, which include poly(tetrafluoroethlyene), poly(trifluorochloroethylene), poly(vinylidene fluoride, poly(trifluorochloroethylene-co-vinyl chloride), poly(meth)acrylates or poly(meth)acrylamides containing perfluoroalkyl side groups, and the like. Lubricants useful in the present invention are described in further detail in Research Disclosure No.308, published Dec. 1989, page 1006.

The outermost protective layer useful in the practice of the invention may optionally contain a surface active agent, an antistat agent, a charge control agent, a thickener, a silver halide particle, a polymer latex particle, a colloidal inorganic particle, a magnetic recording particle, and various other additives. The UV layer useful in the practice of the present invention may optionally contain a silver halide particle, an antistat agent, a thickener, a surfactant, a polymer latex particle, and various other additives.

The protective layer useful in the practice of the invention can be applied in any of a number of well-know techniques, such as dip coating, rod coating, blade coating, air knife coating, gravure coating and reverse roll coating, extrusion coating, slide coating, curtain coating, and the like. After coating, the protective layer is generally dried by simple evaporation, which may be accelerated by known techniques such as convention heating. Known coating and drying methods are described in further detail in Research Disclosure No. 308, Published Dec. 1989, pages 1007 to 1008.

The present invention is also directed to a single-use camera having incorporated therein a photographic element as described above. Single-use cameras are known in the art under various names: film with lens, photosensitive material package unit, box camera and photographic film package. Other names are also used, but regardless of the name, each shares a number of common characteristics. Each is essentially a photographic product (camera) provided with an exposure function and preloaded with a photographic material. The photographic product comprises an inner camera shell loaded with the photographic material, a lens opening and lens, and an outer wrapping(s) of some sort. The photographic materials are exposed in camera, and then the product is sent to the developer who removes the photographic material and develop it. Return of the product to the consumer does not normally occur.

Single-use cameras and their methods of manufacture and use are described in U.S. Patent Nos. 4,801,957; 4,901,097; 4,866,459; 4,849,325; 4,751,536; 4,827,298; European Patent Applications 460,400; 533,785; 537,225; all of which are incorporated herein by reference.

The photographic processing steps to which the raw film may be subject may include, but are not limited to the following:

(1) color developing → bleach fixing → washing/stabilizing;

(2) color developing → bleaching → fixing → washing/stabilizing;

(3) color developing → bleaching → bleach-fixing → washing/stabilizing;

(4) color developing → stopping → washing → bleaching → washing → fixing → washing/stabilizing;

(5) color developing → bleach-fixing → fixing → washing/stabilizing;

(6) color developing → bleaching → bleach-fixing → fixing → washing/stabilizing;

Among the processing steps indicated above, the steps (1), (2), (3), and (4) are preferably applied. Additionally, each of the steps indicated can be used with multistage applications as described in Hahm, U.S. Pat. No. 4,719,173, with co-current, counter-current, and contraco arrangements for replenishment and operation of the multistage processor.

Any photographic processor known to the art can be used to process the photosensitive materials described herein. For instance, large volume processors, and so-called minilab and microlab processors may be used. Particularly advantageous would be the use of Low Volume Thin Tank processors as described in the following references: WO 92/10790; WO 92/17819; WO 93/04404; WO 92/17370; WO 91/19226; WO 91/12567; WO 92/07302; WO 93/00612; WO 92/07301; WO 02/09932; U.S. 5,294,956; EP 559,027; U.S. 5,179,404; EP 559,025; U.S. 5,270,762; EP 559,026; U.S. 5,313,243; U.S. 5,339,131.

The present invention will now be described in detail with reference to examples; however, the present invention should not be limited to these examples.

Examples

Example 1. Preparation of UV dye dispersions

UV-1 is an aqueous dispersion containing 7.5 wt% 3-di-n-hexylaminoallylidene-malononitrile UV absorber, 7.5 wt% 1,4-cyclohexylene dimethylene bis-2-ethylhexanoate high boiling organic solvent, 0.934 wt% Alkanol XC surfactant, and 7.5 wt% gelatin. Small particles are obtained by using a multiple orifice homogenizer at 3500 psi and at 45 °C. The dispersions was sent to a chill chunker and stored at 4 °C until they are remelted for coating. Both UV-2 and UV-3 are prepared in a similar manner. Their compositions are listed in Table 1:

Table 1

UV Dispersion	Composition
UV-1	An aqueous dispersion containing 7.5 wt% 3-di-n-hexylaminoallylidene-malononitrile UV absorber, 7.5 wt% 1,4-cyclohexylene dimethylene bis-2-ethylhexanoate high boiling organic solvent, 0.934 wt% Alkanol XC surfactant, and 7.5 wt% gelatin
UV-2	An aqueous dispersion containing 7.5 wt% propyl 2-cyano-3-(4-methoxyphenyl)-2-propenoate UV absorber, 7.5 wt% 1,4-cyclohexylene dimethylene bis-2-ethylhexanoate high boiling organic solvent, 0.934 wt% Alkanol XC surfactant, and 7.5 wt% gelatin
UV-3	An aqueous dispersion containing 3.75 wt% propyl 2-cyano-3-(4-methoxyphenyl)-2-propenoate UV absorber, 3.75 wt% 3-di-n-hexylaminoallylidene-malononitrile, 5.25 wt% tricresyl phosphate high boiling organic solvent, 0.55 wt% Alkanol XC surfactant, 0.75 wt% Irganox 1076*, and 10 wt% gelatin

* Irganox 1076 is sold by American Cyanamide

Example 2. Preparation of modified gelatin:

To a 12.5% solution of lime processed gelatin at 50 °C. is added ethylenediamine dihydrochloride at 48 mol% based on the moles of carboxyl groups (from aspartic and glutamic acid moieties) in dry gelatin. The pH is adjusted to 5.2 with HCl. To this is added with stirring 1-pyrrodinylcarbonyl pyridinium chloride at 15 mol% based on the moles of carboxyl groups in dry gelatin. The mixture is stirred for 23 hours at approximately 60 °C., then is chilled and noodled-washed (104 cycles). The resulting modified gelatin is melted, and treated with Proxel GXL preservative, and its pH is adjusted to 5.78.

Preparation of the photographic element:

A series of photographic elements are prepared as follows: A poly(ethylene naphthalate) support having an antihalation layer on one side and an antistatic layer overcoated with a transparent magnetic recording layer on the other side is coated on the antihalation layer with the following imaging forming layers in sequence.

Interlayer: This layer comprises 2,5-di-t-octyl-1,4-dihydroxy benzene (0.075 g/m^2), tri(2-ethylhexyl)phosphate (0.113 g/m^2), and gelatin (0.86 g/m^2).

Slow Cyan Dye-forming Layer: This layer comprises a red sensitive silver bromoiodide emulsion (3.3 mole percent iodide) (0.324 μm grain size) (0.387 g/m^2 silver), compound CC-1 (0.355 g/m^2), IR-4 (0.011 g/m^2), B-1 (0.075 g/m^2), S-2 (0.377 g/m^2), S-3 (0.098 g/m^2), and gelatin (1.64 g/m^2).

Mid Cyan Dye-forming Layer: This layer comprises a blend of a red sensitive silver bromoiodide emulsion (3.3 mole percent iodide) (0.488 μm grain size) (0.816 g/m^2 silver) and a red sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (0.98 μm diameter by 0.11 μm thick) (0.215 g/m^2 silver), compound CC-1 (0.183 g/m^2), IR-3 (0.054 g/m^2), B-1 (0.027 g/m^2), CM-1 (0.011 g/m^2), S-2 (0.183 g/m^2), S-3 (0.035 g/m^2), S-5 (0.054 g/m^2), and gelatin (1.35 g/m^2).

Fast Cyan Dye-forming Layer: This layer comprises a red sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (1.10 μm diameter by 0.11 μm thick) (1.08 g/m^2 silver), compound CC-1 (0.161 g/m^2), IR-3 (0.038 g/m^2), IR-4 (0.038 g/m^2), CM-1 (0.032 g/m^2), S-2 (0.237 g/m^2), S-5 (0.038 g/m^2), and gelatin (1.35 g/m^2).

Interlayer: This layer comprises 2,5-di-t-octyl-1,4-dihydroxy benzene (0.075 g/m^2), tri(2-ethylhexyl)phosphate (0.113 g/m^2), and gelatin (0.86 g/m^2).

Slow Magenta Dye-forming Layer: This layer comprises a blend of a green sensitive, tabular grain, silver bromoiodide emulsion (1.5 mole percent iodide) (0.7 μm diameter by 0.112 μm thick) (0.258 g/m^2 Ag), and a green sensitive, tabular grain, silver bromoiodide emulsion (1.3 mole percent iodide) (0.54 μm diameter by 0.086 μm thick) (0.409 g/m^2 Ag), compound M-1 (0.204 g/m^2), MM-1 (0.038 g/m^2), ST-1 (0.020 g/m^2), S-1 (0.26 g/m^2), and gelatin (1.18 g/m^2).

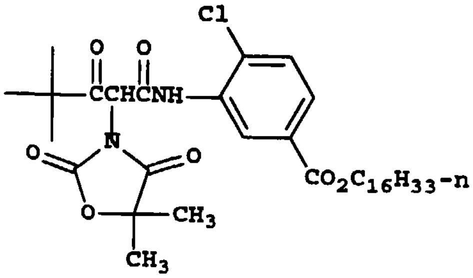
Mid Magenta Dye-forming Layer: This layer comprises a green sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (0.61 μm diameter by 0.12 μm thick) (0.646 g/m^2 Ag), compound M-1 (0.099 g/m^2), MM-1 (0.027 g/m^2), IR-2 (0.022 g/m^2), ST-1 (0.010 g/m^2), S-1 (0.143 g/m^2), S-2 (0.044 g/m^2), and gelatin (1.41 g/m^2).

Fast Magenta Dye-forming Layer: This layer comprises a green sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (0.98 μm diameter by 0.113 μm thick) (0.699 g/m^2 Ag), compound M-1 (0.052 g/m^2), MM-1 (0.032 g/m^2), IR-2 (0.022 g/m^2), ST-1 (0.005 g/m^2), S-1 (0.111 g/m^2), S-2 (0.044 g/m^2), and gelatin (1.123 g/m^2).

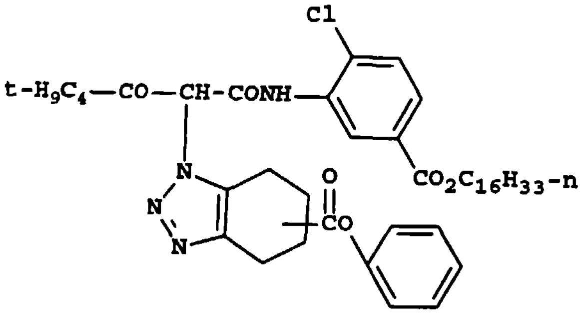
Yellow Filter Layer: This layer comprises 2,5-di-t-octyl-1,4-dihydroxy benzene (0.075 g/m^2), YD-2 (0.108 g/m^2), Irganox 1076 sold by Ciby Geigy (0.01g /m^2), S-2 (0.121 g/m^2) and gelatin (0.861 g/m^2).

Slow Yellow Dye-forming Layer: This layer comprises a blend of a blue sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (1.4 μm diameter by 0.131 μm thick) (0.161 g/m^2 Ag), a blue sensitive, tabular grain, silver bromoiodide emulsion (1.5 mole percent iodide) (0.85 μm diameter by 0.131 μm thick) (0.0.108 g/m^2 Ag), and a blue sensitive, tabular grain, silver bromoiodide emulsion (1.3 mole percent iodide) (0.54 μm diameter by 0.086 μm thick) (0.161 g/m^2 Ag), compound Y-1 (0.915 g/m^2), IR-1 (0.032 g/m^2), B-1 (0.0065 g/m^2), S-1 (0.489 g/m^2), S-3 (0.0084 g/m^2), and gelatin (1.668 g/m^2).

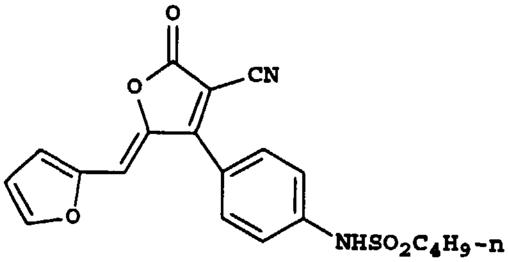
Fast Yellow Dye-forming Layer: This layer comprises a blue sensitive, tabular grain, silver bromoiodide emulsion (4.5 mole percent iodide) (2.3 μm diameter by 0.128 μm thick) (0.43 g/m^2 Ag), compound Y-1 (0.15 g/m^2), IR-1 (0.032 g/m^2), B-1 (0.0054 g/m^2), S-1 (0.091 g/m^2), S-3 (0.0070 g/m^2), and gelatin (0.753 g/m^2).



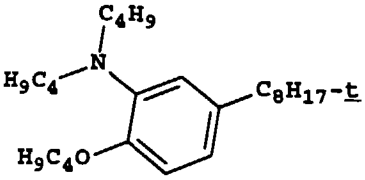
Y1



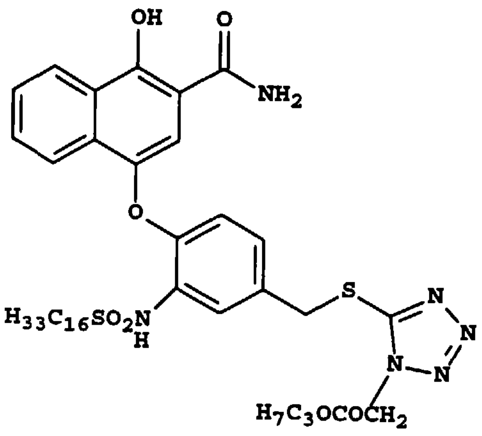
IR-1



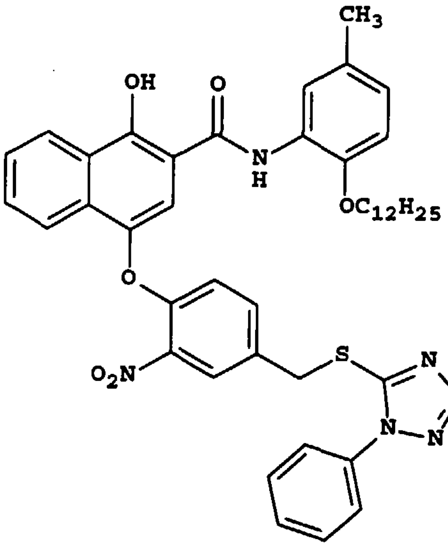
YD-2



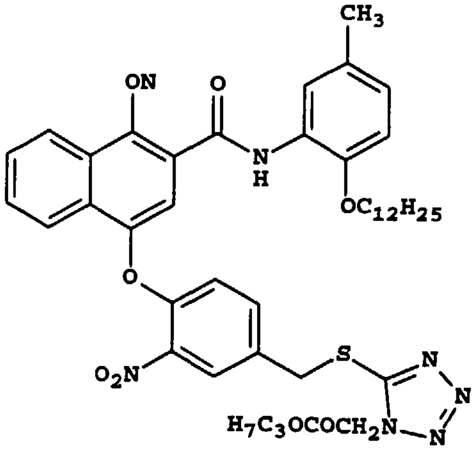
ST-1



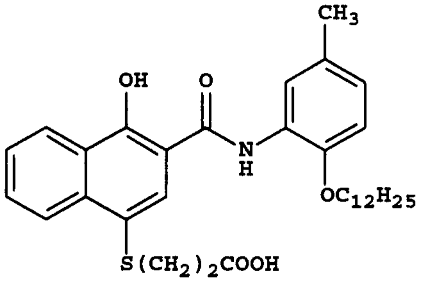
IR-2



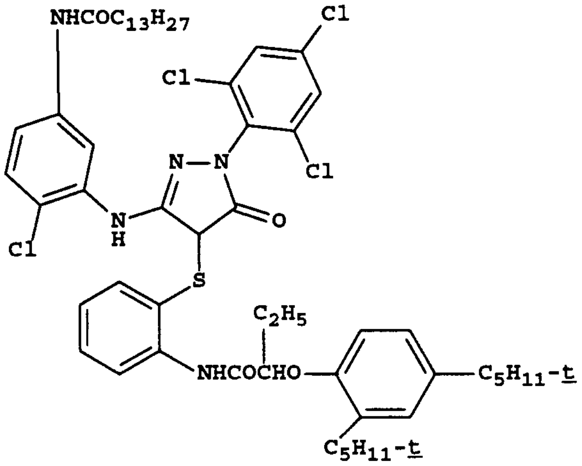
IR-3



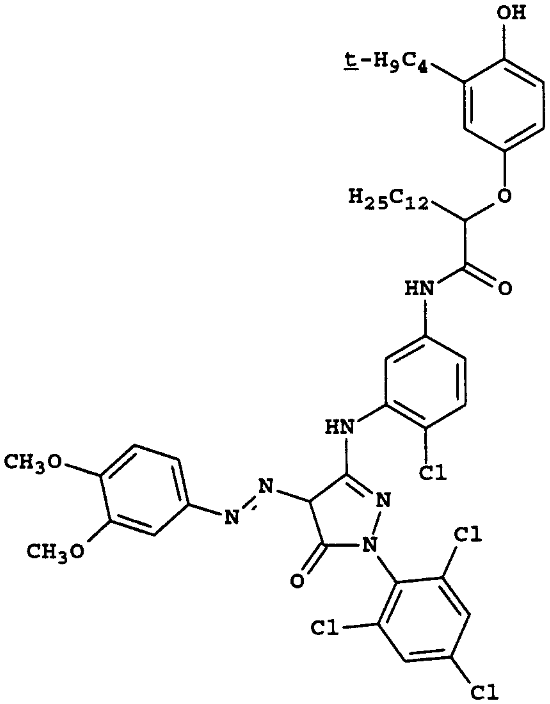
IR-4



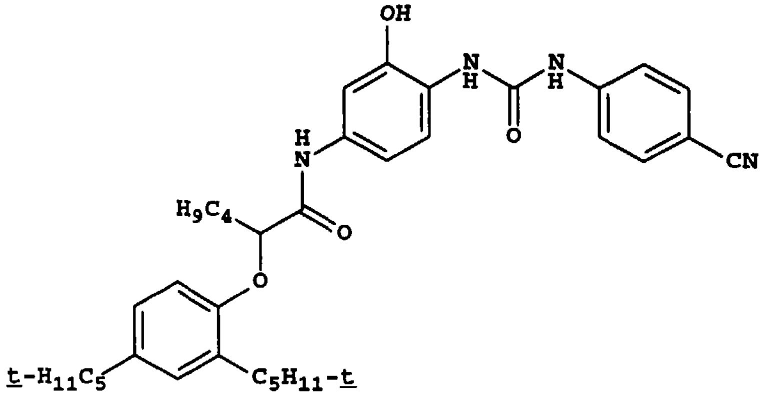
B-1



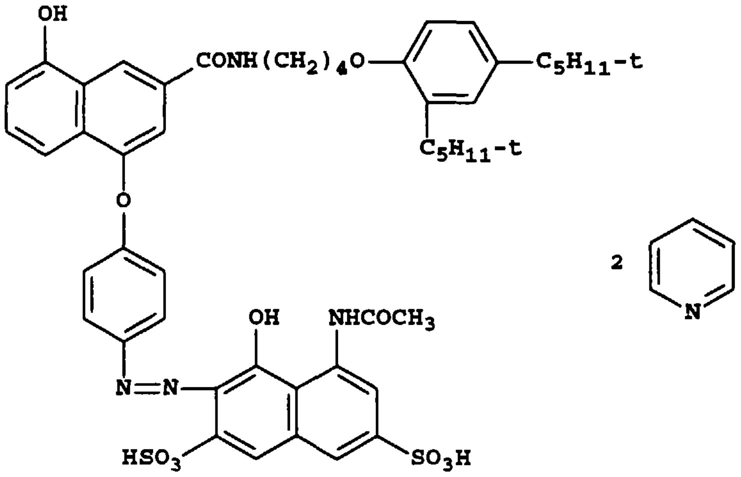
M-1



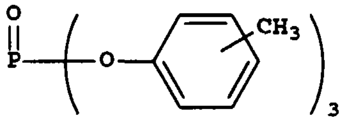
MM-1



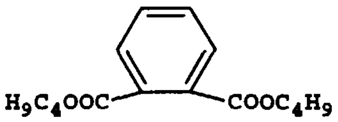
CC-1



CM-1



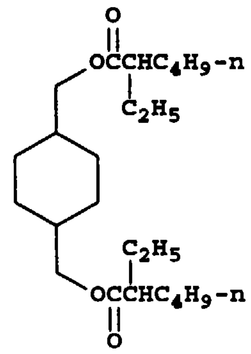
S-1



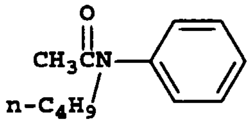
S-2

$C_{11}H_{23}CON(C_2H_5)_2$

S-3



S-4



S-5

The UV layer is prepared according to the composition in Table 2 and coated on the top of the fast yellow dye forming layer. The outermost layer is prepared according to the composition in Table 3 and coated on the top of the UV layer.

In forming the UV layer of the present invention, the UV-1, UV-2, and UV-3 dispersions are used to form the coating solutions. The coating examples are presented in terms of dry coating compositions.

Table 2

Composition of the UV layer	
Gelatin, lime processed	0.7 g/m^2
Colloidal Silver	0.215 g/m^2
High boiling organic solvent HS-1 or HS-2	in Table 4
UV Dye-1	in Table 4
UV Dye-2	in Table 4

HS-1: 1,4-cyclohexylene dimethylene bis-2-ethylhexanoate
HS-2: tricresyl phosphate
UV Dye-1: 3-di-n-hexylaminoallylidene-malononitrile
UV Dye-2: propyl 2-cyano-3-(4-methoxyphenyl)-2-propenoate

Table 3

Composition of the outermost Layer	
Gelatin, see Table 4	0.89 g/m^2
Silicone lube, DC-200 (Dow Corning)	0.04 g/m^2
Fluorad FC-134	0.004 g/m^2
Aerosol OT	0.0215 g/m^2
Surfactant Olin 10G	0.0273 g/m^2
Matte 1: Poly(vinyl toluene-co-divinyl benzene) 80:20 wt%, 1.5 μm	see Table 4
Matte 2: Poly(vinyl toluene-co-divinyl benzene) 80:20 wt%, 0.8 μm	see Table 4
Matte 3: Poly(methyl methacrylate-co-methacrylic acid) 45:55 wt%, 2.7 μm	0.108 g/m^2

Table 4 shows the compositions of the UV and outermost layers of each photographic element prepared.

To evaluate the abrasion and scratch resistance of the protective overcoat, discs of coatings after processing are placed on a Taber Abrader and abraded in accordance with ASTM method D1044. Since the outermost layer contains matting agents, the measurement based on percentage light transmission or difference in percentage haze (Delta Haze) before and after Taber abrasion cannot be used to measure the abrasion resistance of the coatings. Instead, a Gould Microtopographer 200 is used to measured the surface roughness within the track area of the samples after Taber abrasion. The surface roughness is then analyzed in terms of two parameters: PPCM which counts the number of scratches produced by Taber wheels per centimeter and Ra which acounts for the average surface roughness. The product of the two (Ra x PPCM) is used here to quantify how badly the sample surface is scratched. If Ra x PPCM value is greater than 10, the scratch resistance of the samples is poor; if Ra x PPCM value is greater or than equal to 5 and less than 10, the scratch resistance of the samples is good; if Ra x PPCM value is less than 5, the scratch resistance of the samples is excellent. The results are summarized in Table 4.

Table 4

Coating No	Outermost Layer			UV Layer			Scratch Resist.
	Gelatin/H [a]	Colloidal Silica[b] mg/m^2	Matte mg/m^2	UV-Dye1 g/m^2	UV-Dye2 g/m^2	H. B. Solvent g/m^2	
Example 3 (Comparative)	Lime processed/1.8% H	10	Matte1 : 5.4	0.106	0.106	HS-1 0.212	Poor
Example 4 (Comparative)	Lime processed/2.1% H	10	Matte1 : 5.4	0.106	0.106	HS-1 0.212	Poor
Example 5 (Comparative)	Lime processed/2.4% H	10	Matte1 : 5.4	0.106	0.106	HS-1 0.212	Poor
Example 6 (Comparative)	Lime processed/1.8% H	-	Matte1 : 10.8	0.106	0.106	HS-2 0.151	Good
Example 7 (Invention)	Lime processed (Modified) [c]/ 1.8% H	-	Matte1 : 10.8	0.106	0.106	HS-2 0.151	Excell.
Example 8 (Comparative)	Lime processed/1.8% H	-	Matte1 : 53.8 Matte2 161.5	0.106	0.106	HS-12 0.151	Good
Example 9 (Invention)	Lime processed (Modified) [c]/ 1.8% H	-	Matte1 : 53.8 Matte2 : 161.5	0.106	0.106	HS-12 0.151	Excell.

[a] H is bis(vinylsulfonyl) methane hardener, and its concentration is based on dry gelatin.

[b] Ludox AM from DuPont de Nemours and Co.

[c] Modified gelatin prepared as in Example 2.

Comparative Examples 3 to 5 contain different amount of bis(vinylsofonyl) methane hardener, and no effect is seen on the scratch resistance of the outermost protective layer. Comparative examples 6 and 8 contain less amount of high boiling organic solvents in the UV layer and therefore their outermost protective layers show good scratch resistance. Invention Examples 7 and 9 contain the same amount of high boiling organic solvents in their UV layer as Comparative Example 6 and 8. However, the use of the modified gelatin in their outermost protective layer in accordance with the present invention has improved significantly the scratch resistance of the outermost protective layer.

Claims

1. A photographic element comprising

a support
at least one light-sensitive layer, and
a light-insensitive protective layer comprising

a UV ray absorbing layer closer to the support containing a UV ray absorbing dye, a high boiling point organic solvent, and a hydrophilic binder,
an outermost protective layer containing a process surviving matting agent and a modified gelatin where at least one carboxylic acid moiety of gelatin is modified into a monoamide of a polyamine whereby at least

one additional amine group is introduced.

2. The photographic element according to claim 1, wherein the hydrophilic binder in the UV absorbing layer has a content of from 30 to 90%.

3. The photographic element according to claim 1, wherein the process surviving matting agent contains particles having a mean particle size of from 0.5 to 10 µm.

4. The photographic element according to claim 1, wherein the UV ray absorbing layer has a thickness of from 0.2 to 3 µm.

5. The photographic element according to claim 1, wherein the protective layer has a thickness of from 0.4 to 3 µm.

6. The photographic element according to claim 1, wherein the UV ray absorbing dye is selected from the group consisting of thiazolidines, benzotriazoles, cinnamic acid esters, benzophenones and aminobutadienes.

7. The photographic element according to claim 1, wherein the high boiling point organic solvent is selected from the group consisting of phthalic esters, phosphonate esters, alcohols, phenols, and aliphatic carboxylate esters.

8. The photographic element according to claim 1, wherein the protective layer includes a lubricant.

9. The photographic element according to claim 1, wherein the protective layer includes an antistat agent.

10. The photographic element according to claim 1, wherein the modified gelatin results from 1 to 40% of the carboxylic acid moieties in a gelatin being modified into monoamides of a polyamine.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 1695

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO 91 20014 A (EASTMAN KODAK CO) 26 December 1991 * the whole document * ---	1-10	G03C1/76 G03C1/815 G03C1/047
A	EP 0 614 930 A (AGFA GEVAERT NV) 14 September 1994 ---	1-10	
A	GB 1 477 410 A (FUJI PHOTO FILM CO LTD) 22 June 1977 * page 17, line 8 - line 13 * ---	1-10	
A	US 4 181 527 A (KOIZUMI JUNJI ET AL) 1 January 1980 * column 1, line 40 - line 50 * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 September 1997	Bolger, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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