# United States Patent

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## [54] NOVEL MORDANT COMPOSITIONS AND PHOTOGRAPHIC ELEMENTS CONTAINING SAME

**4 Claims, No Drawings**


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[50] **Field of Search** ..... 96/84 A, 114, 84, 87



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| 3,282,699 | 11/1966 | Jones et al. | 96/84 |
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**ABSTRACT:** A gelatin composition comprising a basic mordant and an acrylic interpolymer which comprises units of an alkyl acrylate and from about 5 to about 30 weight percent of an ethenic monomer containing a solubilizing group. In one aspect, this invention relates to relatively insoluble photographic elements having antihalation undercoats of said composition which provide strong adherency between film supports and photographic emulsion layers during developing processes.

# NOVEL MORDANT COMPOSITIONS AND PHOTOGRAPHIC ELEMENTS CONTAINING SAME

This invention relates to novel compositions and to photographic elements containing said compositions. In one aspect, this invention relates to a novel composition comprising a basic mordant and an acrylic interpolymer having a specified range of solubilizing groups therein. In another aspect this invention relates to a novel photographic element comprising a support, an antihalation layer containing said composition, and a silver halide layer adjacent said antihalation layer.

It is known that compositions containing basic mordants can be used in various layers of photographic elements to provide bleachable light-screening layers or backing layers. The conventional mordant layers of the prior art generally contain a hydrophilic colloidal material such as gelatin, collodion, hydroxy ethyl cellulose, polyvinyl alcohol, etc., as binder materials. These compositions are often undesirable for use in photographic elements since their use results in low tenacity of adjoining layers, low dimensional stability, cracking, high solubility in basic processing solutions, etc., for example, these inadequacies are especially apparent when mordant layers are coated contiguous with polyester supports, such as a polyethylene terephthalate film, commonly used in photographic elements.

Therefore, it is an object of this invention to provide novel compositions containing basic mordants.

It is another object of this invention to provide a novel composition wherein the basic mordant is compatible with the binder vehicle.

It is another object of this invention to provide a novel composition wherein the basic mordant is compatible with the binder vehicle and said composition can be coated contiguous with a wide variety of photographic film supports without cracking upon aging.

It is another object of this invention to provide novel compositions which contain release mordants which have high tenacity to photographic film supports.

It is another object of this invention to provide novel compositions which contain release mordants which have high tenacity to polyethylene-terephthalate-type film supports and will not wash off the support when processing in basic processing solutions.

It is still another object of this invention to provide novel compositions which can be used as interlayers in photographic elements.

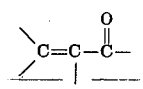
It is a further object of this invention to provide novel photographic elements.

It is still a further object to provide novel photographic elements having bleachable, antihalation interlayers.

These and other objects of the invention are achieved with a composition comprising a basic mordant and an acrylic interpolymer which comprises units of an alkyl acrylate and from 5 to 30 weight percent of units having a water-solubilizing group thereon. Typical of water-solubilizing groups essential in this invention are sulfoester groups, sulfonic acid groups and carboxylic acid groups. In one embodiment the composition is coated on a support, such as polyethylene terephthalate, and silver halide emulsion layers are coated thereon. In this embodiment the composition comprising the release mordant generally contains an acid dye which will provide an antihalation layer which can be treated to release the dye from the mordant whereby a bleachable antihalation layer is obtained. The present composition forms a tenacious bond with most photographic supports, is resistant to cracking and provides good dimensional stability with respect to the support. In the preferred embodiments, release mordants having quaternary heterocyclic groups are utilized and in particular, vinyl polymers having quaternary heterocyclic groups thereon are utilized.

The interpolymers which can be used according to this invention are acrylic interpolymers, i.e., those polymers prepared from polymerizable acrylic monomers containing the characteristic acrylic group





. Such polymers are conveniently prepared by interpolymerization of an acrylic polymer with at least one dissimilar monomer which can be another acrylic monomer or some other different polymerizable ethylenically unsaturated monomer.

The acrylic interpolymers of this invention comprise units of at least one alkyl acrylate and from about 5 to about 30 percent, by weight, of ethenic units having a solubilizing group percent, Typical solubilizing groups which provide substantial compatibility of the acrylic polymer with gelatin and with the basic mordants and still yield a system which is resistant to cracking and has high tenacity to a number of photographic film supports are the sulfoester groups, sulfonic acid groups and the carboxylic acid groups. The interpolymers of this invention preferably are compatible with gelatin and have a Tg (glass transition temperature) of less than 20° C. (Tg can be calculated by differential thermal analysis as disclosed in "Techniques and Methods of Polymer Evaluation", Vol. 1, Marcel Dekker Inc., N.Y., 1966).

Typical alkyl acrylates which may be used in making copolymers are methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylates (e.g. n-butyl or t-butyl acrylate), amyl acrylates, hexyl acrylates and the like.

Solubilizing groups are necessary on at least about 5 to not more than about 30 percent of the units, by weight, in the interpolymer and preferably from about 7 to about 20 percent. Interpolymers having less than about 5 weight percent of the units having solubilizing groups tend to coagulate in a gelatino emulsion containing a basic mordant resulting in a very nonuniform, opaquelike emulsion which cannot be easily coated and which is generally not useful in photographic elements. If more than 30 percent by weight of units having the solubilizing group is present, the composition becomes too soluble to withstand contact with processing solutions and strips away from the support or adjacent layer. This problem is especially prevalent when processing in a basic medium. Thus, the concentration of solubilizing groups in the acrylic interpolymer must be limited, especially when using the composition as an interlayer in a photographic element. Acrylic interpolymers having the above constituency are generally hydrophobic or immiscible with water and form a latex therein. In a preferred embodiment of the invention, interpolymers which are substantially immiscible in water and form a latex therein are utilized to obtain good adhesion and cracking resistance to a polyethylene terephthalate support. Typical polymers useful in this invention are copoly(methyl acrylate-sulfopropyl acrylate), copoly(ethyl acrylate-sulfopropyl acrylate), copoly (butyl acrylate-sulfopropyl acrylate), copoly (methyl acrylate-acrylic acid), copoly (ethyl acrylate-acrylic acid), copoly (butyl acrylate-acrylic acid), copoly (methyl acrylate-3-acryloyloxy-1-methylpropane-1-sulfonic acid, sodium salt), copoly (ethyl acrylate-3-acryloyloxy-propane-1-sulfonic acid) and the like.

In another embodiment of this invention, the above mentioned copolymers contain units of a third monomer. Exceptionally good results are obtained in the process of this invention when the synthetic polymers comprise units of (1) alkyl acrylates, (2) acrylic acid, monomers containing sulfonic acid or sulfoester groups, and (3) an acrylic monomer unit having active methylene groups in side chains such as in malonic ester groups or 1,3-diketone and/or sulfobetaine units. Typical polymers of this class include copoly(ethyl acrylate-acrylic acid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate), copoly (n-butyl acrylate -N-cyanoacetyl-N'-methacrylyl-hydrazine acrylic acid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate), copoly (n-butyl acrylate-2-acetoacetoxyethyl acrylate-acrylic acid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate), copoly (butyl acrylate-acrylic acid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate), and the like. The useful synthetic

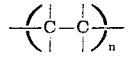
polymers must, of course, be compatible with the components of the antihalation layer.

The acrylic interpolymer generally comprises at least 10 percent to 99 percent, by weight, of the binder vehicle for the emulsion, exclusive of the mordant. In the preferred embodiments, the binder vehicle comprises from about 25 to about 75 percent of the acrylic interpolymer and from about 75 percent to about 25 percent, by weight, gelatin of the total binder vehicle.

The mordants which are useful according to the present invention are generally basic mordants, i.e., those which will combine with or become mordanted to a dye having an acid function thereon. Typical mordants of this type are disclosed in Minsk, U.S. Pat. No. 2,882,156, issued Apr. 14, 1959; Jones, U.S. Pat. No. 3,282,699, issued Nov. 1, 1966; Mader et al, U.S. Pat. No. 3,016,306, issued Jan. 9, 1962; Williams U.S. Ser. No. 480,111, filed Aug. 16, 1965, now U.S. Pat. No. 3,444,138 issued May 13, 1969; and Haseltine et al, U.S. Ser. No. 479,762, filed Aug. 16, 1965, now U.S. Pat. No. 3,455,693, issued July 15, 1969.

The preferred mordants which are especially useful according to the present invention are the basic mordants which will release a mordanted dye upon a simple treatment with a simple solution used in the photographic industry, for example, preferred mordants according to this invention can be treated with an alkali solution to destroy their dye-mordanting capacity resulting in a mordant which will not easily recombine with an acid dye. These preferred mordants are referred to hereinafter as alkali release mordants.

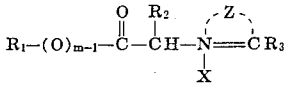
Typical preferred polymeric mordants which are compatible with the acrylic interpolymers are generally ethenic polymers having mordanting groups thereon. These polymers contain a



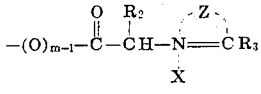
backbone and are generally derived from ethylenically unsaturated monomers, i.e., such as olefin monomers.

In the photographic elements wherein the mordant composition of this invention is used as an interlayer between silver halide emulsions and the support, polymeric and non-polymeric mordants having quaternary heterocyclic groups are preferred. Mordants of this type can be treated with a simple solution such as an alkali solution to destroy the dye-mordanting property of the compound. They generally are not reactivated during normal processing steps to a form wherein they can recombine with acid dyes.

The quaternary nitrogen compounds to be used in the invention include those represented by the following general formula:



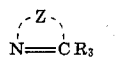
wherein *m* represents an integer of from 1 to 2, $R_1$ represents an alkyl group having typically from one to 18 carbon atoms (e.g., methyl, ethyl, propyl, butyl, hexyl, benzyl, phenethyl, decyl, dodecyl, octadecyl, etc.), or an aryl group (e.g., phenyl, tolyl, naphthyl, diphenyl, terphenyl, etc.), or an amino or substituted group (e.g., amino, dimethylamino, anilino, etc.) or a linear ethenic polymeric structure, for example, an addition type polymer such as a polymer of a monoethylenically unsaturated polymerizable compound having periodically occurring groups of the structure:



attached to carbon atoms in the polymeric chain of a monoethylenically unsaturated polymer (e.g., a polyvinyl ester or alkyl ketone, a polyisopropenyl ester or alkyl ketone), the said chain may also include units of vinyl alcohol, unquaternized vinyl ester or vinyl alkyl ketone; $R_2$ represents the hydrogen atom, a lower alkyl group (e.g., methyl, ethyl, etc.), or a phenyl group; $R_3$ represents the hydrogen atom, an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl, pentadecyl, benzo, phenethyl, etc.), a hydroxyl, a halogen (e.g., chlorine or bromine), or an aryl group (e.g., phenyl, tolyl, biphenylyl, etc.), *X* represents an acid anion (e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, methyl sulfate, ethyl sulfate, p-toluenesulfonate, etc.), and Z represents the nonmetallic atoms required to complete a nucleus containing a five- to six-membered heterocyclic ring having nitrogen, oxygen, sulfur, and selenium as the hetero atoms, typically a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 5-methylthiazole, 5-phenylthiazole, 4,5-dimethylthiazole, 4,5-diphenylthiazole, 4-(2-thienyl)thiazole, etc.), a benzothiazole nucleus (e.g., benzothiazole, 4-chlorobenzothiazole, 5-chlorobenzothiazole, 6-chlorobenzothiazole, 7-chlorobenzothiazole, 4-methylbenzothiazole, 5-methylbenzothiazole, 5-methylbenzothiazole, 5-bromobenzothiazole, 6-bromobenzothiazole, 4-phenylbenzothiazole, 5-phenylbenzothiazole, 4-methoxybenzothiazole, 5-methoxybenzothiazole, 6-methoxybenzothiazole, 5-iodobenzothiazole, 6-iodobenzothiazole, 4-ethoxybenzothiazole, 5-ethoxybenzothiazole, tetrahydrobenzothiazole, 5,6-dimethoxybenzothiazole, 5,6-dioxymethylenebenzothiazole, 5-hydroxybenzothiazole, 6-hydroxybenzothiazole, etc.); a thianaphtheno-7′, 6′, 4, 5-thiazole nucleus, (e.g., 4′-methoxythianaphtheno-7′, 6′, 4,5-thiazole, etc.), an oxazole (e.g., 5-methyloxazole, 4-phenyloxazole, 4,5-diphenyloxazole, 4-ethyloxazole, 4,5-dimethyloxazole, 5-phenyloxazole, etc.), a benzoxazole nucleus (e.g., benzoxazole, 5-chlorobenzoxazole, 5 -methylbenzoxazole, 5-phenylbenzoxazole, 6-methylbenzoxazole, 5,6-dimethylbenzoxazole, 4,6-dimethylbenzoxazole, 5-methoxybenzoxazole, 5-ethoxybenzoxazole, 6-chlorobenzoxazole, 5-hydroxybenzoxazole, 6-hydroxybenzoxazole, etc.), a naphthoxazole nucleus (e.g., α-naphthoxazole, ββ-naphthoxazole, β-naphthoxazole, etc.), a selenazole nucleus (e.g., 4-methylselenazole, 4-phenylselenazole, etc.), a benzoselenazole nucleus (e.g., benzoselenazole, 5-chloroselenazole, 5-methoxybenzoselenazole, 5-hydroxybenzoselenazole, tetrahydrobenzoselenazole, etc.), a naphthoselenazole nucleus (e.g., α-naphthoselenazole, β, β-naphthoselenazole, β-naphthoselenazole, etc.), a thiazoline nucleus (e.g., thiazoline, 4-methylthiazoline, etc.), a quinoline nucleus (e.g., quinoline, 3-methylquinoline, 5-methylquinoline, 7-methylquinoline, 8-methylquinoline, 6-chloroquinoline, 8-chloroquinoline, 6-methoxyquinoline, 6-ethoxyquinoline, 6-hydroxyquinoline, 8-hydroxyquinoline, etc.), an isoquinoline nucleus (e.g., isoquinoline, 3-methylisoquinoline, 5-methylisoquinoline, 6-chloroisoquinoline, 6-methoxyisoquinoline, 8-hydroxyisoquinoline, etc.), a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine, 3,3,5-trimethylindolenine, 3,3,7-trimethylindolenine, etc.), a pyridine nucleus (e.g., pyridine, 2-methylpyridine, 2-benzylpyridine, 3-chloropyridine, 3-hydroxypyridine, 2-methyl-5-ethylpyridine, 2,5-dibutylpyridine, 3-diphenylmethylpyridine, 4-diphenylmethylpyridine, hydroxydiphenylmethylpyridine, etc.), an imidazole nucleus (e.g., imidazole, 1-alkyl imidazole, 1-alkyl-4-phenylimidazole, 1-alkyl-4,5-dimethylimidazole, etc.), a benzimidazole nucleus (e.g., benzimidazole, 1-alkylbenzimidazole, 1-aryl-5,6-dichlorobenzimidazole, etc.), a naphthimidazole nucleus (e.g., 1-alkyl-α-naphthimidazole, 1-aryl-β-naphthimidazole, 1-alkyl-5-methoxy-α-naphthimidazole, etc.), a 1,2,4-thiadiazole nucleus, a 1 or 4 alkyl-1,2,4-triazole nucleus (e.g., 1-methyl-1,2,4-triazole, 1-butyl-1,2,4-triazole, 4-ethyl-1,2,4-triazole, etc.), a tetrazole nucleus (e.g., tetrazole, 5-methyl-1,2,3,4-tetrazole, 5-phenyl-1,2,3,4-tetrazole, etc.), and the like nuclei.

The preferred polymeric release mordants containing

quaternary nitrogen compounds are prepared by reacting a polymeric compound, such as polyvinyl chloroacetate or copolymers containing vinyl chloroacetate, with a heterocyclic tertiary amine having the general formula:



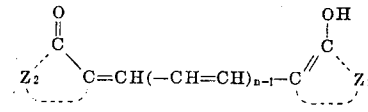
wherein $R_3$ and Z are above defined. A typical process is described in Williams U.S. Ser. No. 480,111, filed Aug. 16, 1965, now U.S. Pat. No. 3,444,138. The quaternary salt products consisting of from about 25 to about 100 percent by weight, of quaternized units and from about 15–0 percent, by weight, unquaternized residual units have been found to be especially efficacious mordants in photographic compositions and are preferred.

The photographic elements prepared with the above described polymeric and nonpolymeric mordants mordants the invention comprise a support material having thereon at least one colloid layer containing an acrylic interpolymer and a basic mordant respectively as defined above. A silver halide can also be included in this layer. However, the preferred light-sensitive photographic elements comprise a support having thereon at least one layer containing said mordants and said acrylic interpolymers and at least one silver halide emulsion layer. Especially good photographic elements are obtained when a polyester support, which can be treated in the conventional manner according to Alles, U.S. Pat. No. 2,570,478, issued Jan. 29,1957 or Nadeau et al., U.S. Pat. No. 3,271,345, issued Sept. 6, 1966, is coated with an antihalation layer comprising said mordants and said acrylic interpolymers; the silver halide layers can be subsequently coated thereon. This preferred embodiment provides an antihalation underlayer having good tenacity to the polyester support, which is resistant to cracking and is compatible with gelatinous overlayers to form an element which can be processed under a variety of conditions.

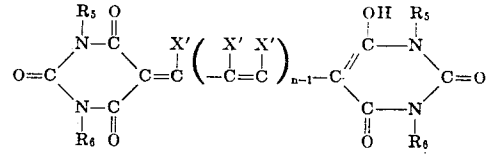
The mordant containing layers are generally prepared by coating on the support or photographic element an aqueous gelatino mixture of the acrylic interpolymer, the basic mordant, and a dye. Surface active agents, as mentioned in U.S. Pat. No. 3,142,568, issued July 28, 1964, can also be included in the coating mixture. Suitable wetting agents include the nonionic, ionic, and amphoteric types as exemplified by the polyoxyalkylene derivatives, amphoteric amino acid dispersing agents, including sulfobetaines and the like. Such wetting agents are disclosed in U.S. Pat. No. 2,600,831, issued June 17, 1952; U.S. Pat. No. 2,271,622, issued Feb. 3, 1942; U.S. Pat. No. 2,271,623, issued Feb. 3,1942; U.S. Pat. No. 2,275,727, issued Mar. 10, 1942 and U.S. Pat. No. 2,787,604, issued Apr. 2,1957; U.S. Pat. No. 2,816,920, issued Dec. 17, 1957; U.S. Pat. No. 2,739,891, issued Mar. 27, 1956, and British Pat. 1,022,878.

Hardening materials that may be used to advantage include such hardening agents as formaldehyde; a halogen-substituted aliphatic acid such as mucobromic acid as described in White, U.S. Pat. 2,080,019, issued May 11, 1937; a compound having a plurality of acid anhydride groups such as 7,8-diphenyl-bicyclo-(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, or a dicarboxylic or a disulfonic acid chloride such as terephthaloyl chloride or naphthalene-1,5-disulfonyl chloride as described in Allen and Carroll, U.S. Pat. Nos. 2,725,294and 2,725,295, both issued Nov. 29, 1955; a cyclic 1,2-diketone such as cyclopentane-1,2-dione as described in Allen and Byers, U.S. Pat. No. 2,725,305, issued Nov. 29, 1955; a bisester of methanesulfonic acid such as 1,2di(methanesulfonoxy)ethane as described in Allen and Laakso, U.S. Pat. No. 2,726,162, issued Dec. 6, 1955; 1,3-dihydroxymethyl-benzimidazole-2-one as described in July, Knott and Pollak, U.S. Pat. No. 2,732,316, issued Jan. 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by two–three carbon atoms, such as β-methyl glutaraldehyde bis-sodium bisulfite as described in Allen and Burness, Canadian Pat. No. 588,451, issued Dec. 8, 1959; a bis-aziridine carboxamide such as trimethylene bis(1-aziridine carboxamide) as described in Allen and Webster, U.S. Pat. No. 2,950,197, issued Aug. 23, 1960; or 2,3-dihydroxydioxane as described in Jeffreys, U.S. Pat. No. 2,870,013, issued Jan. 20, 1959.

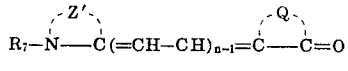
Typical dyes which can be mordanted in accordance with my invention include any filter dye that has one or more acidic group substituents such as sulfo or carboxyl groups, for example, the oxonol dyes described and claimed in copending application of Joseph Bailey, Ser. No. 98,709, filed Mar. 27, 1961, now U.S. Pat. No. 3,247,127, having the formula:



and more particularly the dyes of the formula:



wherein $Z_2$ represents the nonmetallic atoms necessary to complete a 1-carboxyalkyl-3-hydrocarbon substituted hexahydro-2,4,6-trioxo-5-pyrimidine nucleus, *n* in each case is an integer of from 1 to 3, each $R_5$ represents a carboxyalkyl group in which the carboxy substituent is attached to an alkyl group having from one to two carbon atoms, $R_6$ is an alkyl group of from one to eight carbon atoms or an aryl group such as phenyl or an alkyl or alkoxy substituted phenyl group, and X′ is hydrogen or an alkyl group of from one to four carbon atoms, such that no more than one X′ is an alkyl group. Other suitable acid dyes include the benzoxazole-pyrazolone merocyanine dyes described in copending application of Jones et al. U.S. Ser. No. 167,666, filed Jan. 22, 1962, now U.S. Pat. No. 3,282,699, having the formula:



wherein $R_7$ represents an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, etc., or a carboxyalkyl group, such as carboxymethyl, carboxyethyl, carboxypropyl, etc., or a sulfoalkyl group, such as sulfoethyl, sulfopropyl, sulfobutyl, etc.; Z′ represents the nonmetallic atoms necessary to complete a heterocyclic nucleus of the benzoxazole series (including benzoxazole and benzoxazole substituted with substitutions such as methyl, ethyl, phenyl, methoxy, ethoxy, chlorine, bromine, etc.) or a nucleus of the benzoxazole series which has a sulfosubstituent on the benzene ring as well as one or more of the above-mentioned simple substituents, such that when $R_7$ represents an alkyl group, Z′ represents the sulfosubstituted benzoxazole nucleus and when $R_7$ represents a carboxyalkyl group or a sulfoalkyl group, Z′ represents the nonmetallic atoms necessary to complete a benzoxazole nucleus; Q represents the nonmetallic

atoms necessary to complete a heterocyclic nucleus of the sulfophenyl pyrazolinone series and *n* is an integer from 1 to 3. However, the invention is not limited to just those dyes coming within the general formula of the above-mentioned copending applications, since as previously set forth any filter dye containing one or more sulfo or carboxyl groups can be employed. For example, the yellow dyes mentioned in Mader et al. U.S. Pat. No. 3,016,306, issued Jan. 9,1962, columns 5 and 6.

Typical light-filtering dyes include, for example, bis(1-butyl-3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine)-pentamethineoxonol, bis(1-carboxymethyl-3-cyclohexylhexahydro-2,4,6-trioxo-5-pyrimidine) pentamethineoxonol, bis(1-butyl -3-carboxymethylhexahydro-2,4,6-trioxo-5-pyrimidine(trimethineoxonol, bis(1-carboxymethylhexahydro-3-octyl-2,4,6-trioxo-5-pyrimidine) methineoxonol, 4-[(3-ethyl-2(3H)-benzoxazolylidine)-ethylidene]- 3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one monosulfonated, 4-[4-(3-ethyl-2(3H)-benzoxazolylidene)-2-butenylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazoline-5-one monosulfonated, 4-[3-β-carboxyethyl-2(3H)-benzoxazolylidene)ethylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one, 4-[4-(3-β-carboxyethyl-2(3H) -benzoxazolylidene)-2-butenylidene]-3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one, bis(1-butyl-3-carboxymethyl-5-barbituric acid)-trimethine oxonol, bis(1-butyl-3-carboxymethyl-5-barbituric acid) pentamethineoxonol, bis[3-methyl-1-(p-sulfophenyl)-2-pyrazoline-5-one-(4)]methineoxonol, bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)]trimethineoxonol, bis[3-methyl-1-(p-sulfophenyl) -2-pyrazolin-5-one-(4)]pentamethineoxonol, bis[3-methyl-1-(p-sulfophenyl)-5-pyrazolene-(4)]pentamethineoxonol, and typical ultraviolet absorbing dyes include the 2,5-bis(substituted sulfophenyl)-thiazolo[5,4-d]thiazole disodium salts of Sawdy, U.S. Ser. No. 183,417, filed Mar. 29, 1962, now U.S. Pat. No. 3,250,617, such as 2,5-bis(o-methoxy-x-sulfophenyl)thiazole [5,4-d]thiazole disodium salt, 2,5-bis (o-hexyloxy-x-sulfophenyl)thiazolo [5,4-d]thiazole disodium salt, 2,5-bis(o-decyloxymethyl-x-sulfophenyl)thiazolo[5,4-d]thiazole disodium salt, 2,5-bis(5-butyl-2-methyl-x-sulfophenyl)thiazolo [5,4-d]thiazole disodium salt, 2,5-bis (m-methyl-x-sulfophenyl) thiazolo[5,4-d]thiazole disodium salt, 2,5-bis(p-propyl-x-sulfophenyl)thiazolo[5,4-d]thiazole disodium salt, etc.; the ultraviolet-absorbing dyes of Sawdey, U.S. Pat. No. 2,739,888, issued Mar. 27, 1956, such as 3-phenyl-2-phenylimino-5-o-sulfobenzal-4-thiazolidone sodium salt, 5-(4-methoxy-3-sulfobenzal)-3-phenyl-2-phenylimino-4-thiazolidone (sodium salt), 3-phenyl-2-phenyl-imino-5-[3-(3-sulfobenzimido)-benzal]-4-thiazolidone (sodium salt), 3-benzyl-2-phenylimino-5o-sulfobenzal-4-thiazolidone (sodium salt), 5-(2,4-dicarboxymethoxybenzal)-3-phenyl-2-phenylimino-4-thiazolidone sodium salt, etc., tartrazine, and the like filter dyes.

The mordant-acrylic interpolymer compositions of this invention can be coated on a wide variety of supports. Typical continuous supporting sheets include, for example, cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polycarbonate film, polystyrene film, polyethylene terephthalate film and other polyester film as well as glass, paper, metal, wood and the like. Supports such as paper can be coated with alpha-olefin polymers, particularly polymers of alpha-olefins containing two or more carbon atoms, as exemplified by polyethylene, polypropylene, ethylenebutene copolymers and the like. However, polyester supports, such as polyethylene terephthalate and related linear polyesters made from mixtures of glycols and acid constituents, are preferred in the present invention. Especially good results are obtained when the basic mordant acrylic interpolymer compositions are coated thereon as good structural properties and dimensional stability are achieved in this structural combination.

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 purposes of illustration and are not intended to limit the scope of the invention unless otherwise specifically indicated.

## EXAMPLE 1

A polymeric mordant comprising 40percent, by weight, of recurring (vinyl pyridinium acetate) chloride is prepared by reacting an acetone solution of 20g. of polyvinyl chloroacetate with 40 ml. of pyridine. The soft precipitate is decanted, dissolved in methanol, precipitated in ether, washed and vacuum dried. Sixty percent by weight of the resulting polymer comprised unreacted vinyl chloroacetate units.

The above mordant is then slurred in water and mixed with a 10 percent gelatin solution, chilled, and washed. Then is added 4- chloro 3,5-xylenol at a concentration of 3.3 g. per 100 ml. of the solution.

A dye mixture is prepared by mixing 10 ml. of bis[1-(p-sulfophenyl)-3-methyl-5-pyrazolone-(4)] methine oxonol solution, 40 ml. of bis[1-(p-sulfophenyl)3-methyl-5-pyrozolone-(4)] trimethine oxonol solution, 20ml. of bis[3-methyl-l-p-sulfophenyl-5-pyrazolone-(4)] pentamethineoxonol solution, 101.3 ml. 4-[4-(3-ethyl-2(3H)-benzoxalinylidene)-2-butenylidene]3-methyl- 1-p-sulfophenyl-2-2-pyrazolin-5-one 902.5monosulfonated, 90 ml. saponin solution, 630 ml. distilled water and 9 ml. of 2.5 N sodium hydroxide.

The following samples are made using the above mordant composition, the above dye solution and the following acrylic interpolymer composition. To 151grams of the mordant mixture is added 61 grams of 10 percent gelatin, 94.5 ml. distilled water and 104 milliliters of the dye solution. The mixture is adjusted to a pH of 5.9. 87.5 ml. of a 20 percent solution of copoly(butyl acrylate- sulfopropyl acrylate) (5 percent by weight sulfopropyl acrylate) is added followed by 0.31 ml. 10 percent formaldehyde solution and the mixture is coated on a polyethylene terephthalate film support and dried. A gelatino silver halide layer is coated on top of this layer.

A control sample is made by mixing 151 grams of the mordant mixture with 61 grams of 10 percent gelatin, 182 ml. distilled water and 104 ml. of the dye mixture. The pH is adjusted to 5.9 and 0.31 ml. of 10 percent formaldehyde solution is added. The mixture is coated on a polyethylene terephthalate film support and dried. A gelatino silver halide layer is coated on top of this layer.

Both the control sample and the sample containing the acrylic interpolymer gave clear coatings showing no signs of incompatibility.

The respective coated films are subjected to 4 days of cycling between 5 and 85 percent relative humidity at 160° F. (approximately three full cycles) and the extent of cracking is evaluated; a rating of 7 is considered the worst condition and a rating of O the best, i.e., no cracks.

| Addenda | cracking Test |
|---|---|
| Gelatin (control) | 7 |
| Acrylic Interpolymer | 1-2 |

It is apparent that the layer containing the acrylic interpolymer provides far better physical characteristics in the element than the control sample containing gelatin as the binder vehicle.

A similar composition made with polymethyl methacrylate was not compatible with the release mordant resulting in a coagulated mixture which could not be coated.

## EXAMPLE 2

The cracking and adhesion problems of a basic mordant mixture are more apparent when utilizing a polyethylene terephthalate film support than when using a conventional film support such as cellulose acetate.

A control sample and sample containing copoly(butyl acrylate-sulfopropyl acrylate) prepared according to example 1 are coated respectively on polyethylene terephthalate (PET) and cellulose acetate (CA) supports with the following results when tested according to example 1.

| Sample | Support | Cracking Test |
|---|---|---|
| Gelatin Control | PET | 7 |
| Gelatin Control | CA | 1 |
| Acrylic Interpolymer | PET | 1–2 |
| Acrylic Interpolymer | CA | 3 |

A significant improvement in cracking resistance is obtained when using the basic mordant-acrylic interpolymer composition on polyethylene terephthalate supports. However, it can also be used on other photographic supports.

## EXAMPLE 3

A release mordant composition like the control of example 1 and containing 182 ml. of a 8.9 percent solution of copoly (ethyl acrylate-acrylic acid) (20 percent acrylic acid by weight) and 5.3 ml. of resorcinol bis-glycidyl ether is adjusted to a pH of 6.6 and coated on a polyester support resulting in a clear coating showing no signs of incompatibility. A gelatino silver halide layer is coated on top of this layer.

This sample is compared with a control sample similar to example 1 for pinholes after the humidity-cycling test. The control sample is rated at 7 while the present sample is rated at 3. The present release mordant composition has excellent adhesion to the polyester support. The gelatino silver halide layer coated on the release mordant composition layer adheres well during conventional processing steps.

## EXAMPLE 4

The following samples are prepared by mixing approximately 152 g. of the mordant mixture of example 1, 61 g. of 10 percent gelatin, 104 ml. of the dye mixture, adjusting to a pH of 5.9 and then adding an aqueous solution containing 17.5 g. of the polymer specified below (pH 5.9 and sufficient water to bring the total to 500 g. To this mixture is added 0.31 ml. of a 10 percent aqueous formaldehyde solution and in those samples indicated by (*) 5.3 g. of Resorcinol bis-glycidyl ether. The compositions are coated on polyethylene terephthalate film and tested according to example 1.

A. Copoly(n-butyl acrylate-acrylic acid) (10 percent acrylic acid units by weight)

B. Copoly(ethyl acrylate-acrylic acid-4,4,9-trimethyl -8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate) 10 percent, by weight, sulfonate units)

C. Copoly(n-butyl acrylate-N-cyanoacetyl-N'-methacrylyl-hydrazine-acrylic acid-4,4,9-trimethyl 8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate) (10 percent, by weight, acrylic acid units; 7.50percent, by weight sulfonate units)

D. Copoly(n-butyl acrylate-2-acetoacetoxy ethyl acrylate-acrylic axid-4,4,9-trimethyl-8-oxo-7-oxa-4-azonia-9-decene-1-sulfonate) (10 percent, by weight, acrylic acid units; 7.5percent, by weight, sulfonate units)

E. Copoly(methyl acrylate-3-acryloxypropane-1-sulfonic acid) sodium salt. (10 percent, by weight, sulfonic acid units)

| Addenda | Cracking Test |
|---|---|
| Control | 5–7 |
| A* | 2–3 |
| B* | 2–3 |
| C | 2 |
| D | 3 |
| E | 0–1 |

The presence of the specified acrylic interpolymers reduced cracking without decreasing adhesion in all cases. All of the above layers can be subjected to normal aqueous processing treatments in alkali solutions without dissolving the layer. Mordant compositions comprising acrylic interpolymers having over 30 percent, by weight, of units having solubilizing groups such as carboxylic acid, i.e., polymethacrylic acid, alcohol, sulfonate or sulfonic groups thereon become soluble and wash off in alkali solutions.

Similar results are obtained when the basic mordants, poly(vinyl pyridinium methyl ketone chloride), poly(vinyl quinoliniumacetate chloride), poly(vinyl pyridinium - γ-methylacetate chloride), poly(vinyl methylthiozoliumacetate chloride), poly (vinyl-2-ethylelenazolium acetate chloride), 1-(2'/-hydroxy-4'- pentadecylphenacyl)pyridinium iodide, 4-benzyl-1-(2-phenylphenacyl) pyridinium iodide, and poly(γ-methylallyl-N-quanidylketimine), are used in combination with the acrylic interpolymers.

The invention has been described in considerable detail with 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 as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic element comprising (1) a support (2) a layer comprising a hydrophilic colloid a basic release mordant and an acrylic interpolymer which comprises units of an alkyl acrylate and from about 5 to 30 percent, by weight, of an ethenic monomer containing a free sulfoester group, carboxyl group or a sulfonic acid group and (3) a radiation sensitive emulsion layer.

2. A photographic element according to claim 1 wherein said radiation sensitive layer comprises a gelatino silver halide emulsion.

3. A photographic element according to claim 1 wherein said layer comprising said basic mordant further comprises an acid dye.

4. A photographic element according to claim 1 wherein said support is a linear polyester.

* * * * *

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# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,615,545 Dated October 26, 1972

Inventor(s) Norman W. Kalenda

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

Column 2, line 13, "percent," should read ---thereon.---;

Column 3, line 67, delete "amino," after "e.g.," and insert -- amino -- before "group";

Column 4, lines 23-24, the second "5-methylbenzothiazole" should read ---6-methylbenzothiazole---;

Column 5, line 22, delete the second "mordants" and insert ---of--- after the first "mordants";

Column 8, line 21, "902.5" should be deleted;

Column 9, line 54, "axid" should read ---acid---;

Column 10, line 30, delete "/" after "(2'".

Signed and sealed this 15th day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents