April 20, 1971 D. W. HESELTINE ET AL 3,575,993

CERTAIN PHENACYL PYRIDINIUM COMPOUNDS

Original Filed Aug. 16, 1965

FIG. 1

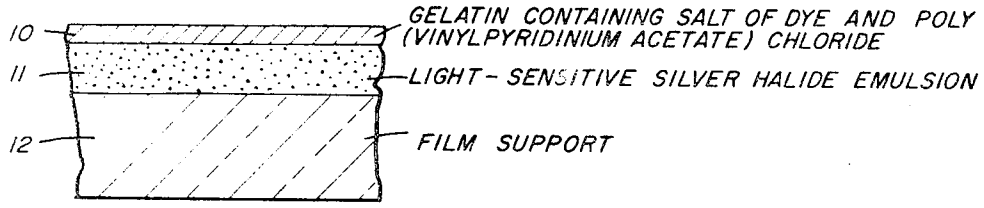


FIG. 2

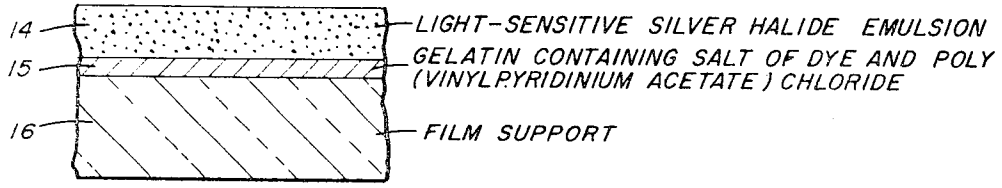
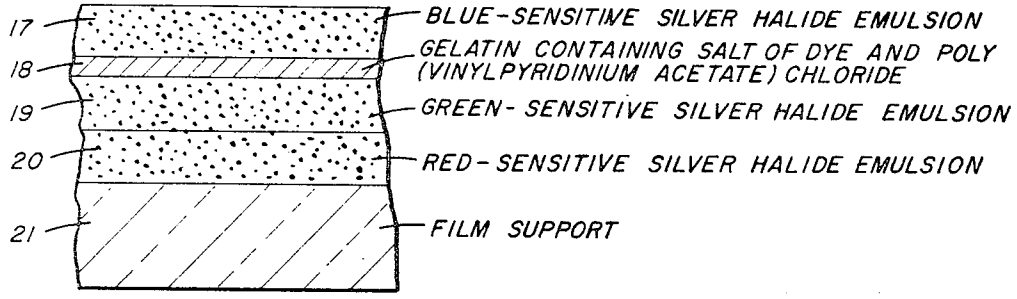


FIG. 3



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3,575,993

CERTAIN PHENACYL PYRIDINIUM COMPOUNDS

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Original application Aug. 16, 1965, Ser. No. 479,762, now Patent No. 3,455,693, dated July 15, 1969. Divided and this application Aug. 9, 1968, Ser. No. 774,552

Int. Cl. C07d 31/28

U.S. Cl. 260—297 8 Claims

ABSTRACT OF THE DISCLOSURE

A bulky quaternary nitrogen heterocyclic alkali-release mordant that under alkaline conditions form a betaine that will not mordant anions, is advantageously used as a mordant for a water-soluble acid dye and hydrophilic colloid light-absorbing and light-filtering layers of photographic elements where it is desired to firmly hold the acid dye until photographic processing when during treatment in the alkaline processing solutions the acid dye is completely released and the betaine formed of the mordant is incapable of remordanting the acid dye or thio-sulfate ions from the fixing bath.

This is a divisional application of U.S. Ser. No. 479,762, "Mordants for Use in Dyed Filter Layers" filed Aug. 16, 1965, now U.S. Pat. 3,455,693, issued July 15, 1969.

This invention relates to certain bulky, i.e., relatively high molecular weight, quaternary nitrogen heterocyclic compounds which function as "alkali-release" mordants, to photographic materials and more particularly to photographic elements containing these compounds in light-screening and light-absorbing layers, and to methods for their preparation.

The use of organic dye containing light-filter and light-absorbing layers in photographic elements is well known, as in the use of mordants which form substantially insoluble salts or otherwise react with water-soluble dyes, to render the dyes non-diffusing. Such dye-mordant light-screening salt may be in a layer overlying a light-sensitive emulsion or overlying two or more light-sensitive emulsions; or it may be in a light sensitive emulsion for the purpose of modifying a light record in such emulsion or for protecting an overlying light-sensitive emulsion or emulsions from the action of light of wavelengths absorbed by such light-screening substance, or it may be in a layer not containing a light-sensitive substance but arranged between two light-sensitive emulsions; or it may be in a layer serving as a backing on an element having one or more light-sensitive emulsions (for example, to reduce halation).

In particular, light-screening substances are often required (a) in overcoatings upon photographic elements to protect the light-sensitive emulsion or emulsions from the action of light which it is not desired to record, (b) in layers arranged between differentially color sensitized emulsions, e.g., to protect red- and green-sensitive emulsions from the action of blue light, and (c) in backings forming the so-called anti-halation layers on either side of a transparent support carrying the light-sensitive emulsion or emulsions.

In most cases and especially where the element contains a color sensitized emulsion or color sensitized emulsions, it is particularly desirable to employ light-screening substances which do not affect the general sensitivity or the color sensitivity of light-sensitive emulsions with which they may come into contact. It is also particularly desirable to employ light-screening substances which do not substantially diffuse from the layers or coatings in which they are incorporated, either during the manufacture of

the element or on storing it or in photographically processing it. Finally it is generally necessary to employ light-screening substances which can readily be rendered ineffective, i.e., decolorized or destroyed and removed prior to or during or after photographic processing. For many purposes it is particularly convenient to employ light-screening substances which are rendered ineffective by one of the photographic baths employed in processing the element after exposure, such as a photographic developing bath or fixing bath.

Numerous substances have been proposed as mordants to prepare the dye-mordant salts used as light-screening and light-absorbing materials for the purposes indicated above. Among the proposed mordants are relatively high molecular weight compounds having ionic charges opposite to those of the particular light-absorbing dye. For example, the dye employed might be an acid dye, in which case the mordant would be a cationic compound. Typical of such proposed mordants are, for example, derived polymers such as the basic reaction products of polyvinylsulfonates and C-aminopyridines as described in D. D. Reynolds et al., U.S. Pats. 2,701,243 and 2,768,078, granted Feb. 1, 1955, and Oct. 23, 1956, respectively. While polymeric mordants such as illustrated by the above-mentioned patents have the advantage of bulky molecules and do function to fix acid dyes in photographic layers, within their particular limitation, they have not been found entirely satisfactory in many applications primarily because these polymeric mordants on alkaline development do not tend to release the dye, i.e., they still retain their mordanting property and, accordingly, not only tend to retain some residual dye as evidenced by background stain or coloration, but more importantly retain, i.e., fix, an appreciable amount of thiosulfate ion in the subsequent hypo processing used to remove unexposed silver halide. This results in relatively poor quality and stability of the produced image. In view of this, it would be very desirable to have an effective mordant available that is free from such disadvantages.

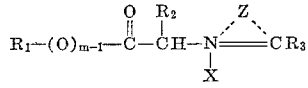
We have now found that certain bulky or relatively high molecular weight quaternary nitrogen heterocyclic compounds are especially useful as precipitants and mordants for acid dyes in photographic layers, and that these compounds, moreover, satisfactorily overcome the above-mentioned shortcomings of heretofore known mordants for this purpose. Thus, our new class of mordants do not retain any residual dye or deleterious amounts of thiosulfate ion in the layers after processing, and further the produced images are of very good quality and of outstanding keeping properties. These novel mordants are soluble in aqueous solutions, for example, in dilute aqueous solutions of acids such as acetic, butyric, lauric, etc., acids. Furthermore, they have good compatibility with various hydrophilic materials such as gelatin and readily form substantially non-diffusible salts with water-soluble acid dyes. In general, they have a molecular weight of about at least 300, although polymeric materials having a molecular weight of 600 to 50,000, and higher, have been found to be particularly useful in our invention.

It is, accordingly, an object of the invention to provide a light-sensitive photograph element having one or more layers containing at least one novel and non-diffusible salt of certain novel quaternary nitrogen heterocyclic mordants with a water-soluble acid dye. Another object is to provide a light filter layer containing at least one of the above salts; which layer may be coated between two or more silver halide emulsion layers in a multilayer element. Another object is to provide a light-sensitive gelatino-silver halide layer containing at least one of the above salts. Another object is to provide photographic elements with an overcoating and/or a backing layer which contain(s) at least one novel non-dif-

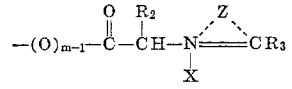
fusing salt of certain novel quaternary nitrogen heterocyclic mordants with water-soluble acid dyes. Other objects will become apparent from consideration of the description and examples.

These and other objects are accomplished according to our invention by the preparation and use of light-sensitive photographic elements with at least one layer containing a non-diffusible light-absorbing salt of a water-soluble acid dye and a new class of bulky quaternary nitrogen heterocyclic compounds of the invention including those represented by the following general formula:

(I)



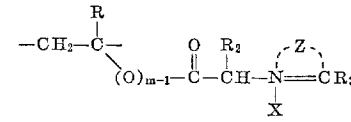
wherein m represents an integer of from 1 to 2, R_1 represents an alkyl group having typically from 1 to 18 carbon atoms (e.g., methyl, ethyl, propyl, butyl, hexyl, benzyl, phenethyl, decyl, dodecyl, octadecyl, etc.), or an aryl group (e.g., phenyl, tolyl, naphthyl, diphenyl, terphenyl, etc.), or an amino or substituted amino group (e.g., amino, dimethylamino, anilino, etc.), or a linear 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 monomethylenically unsaturated polymer (e.g., a polyvinyl ester or alkyl ketone, a polyisopropenyl ester or 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, benzyl, 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 5- to 6-numbered heterocyclic ring having nitrogen, oxygen, sulfur, and selenium as the hetero atoms, typically a thiazole nucleus (e.g., thiazole, 4-methylthiazole, 4-phenylthiazole, 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, 4-methylbenzothiazole, 6-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'-methoxy thianaphtheno-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., benzoxoazole, 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, β,β-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.

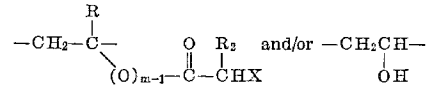
More particularly the new class of bulky quaternary nitrogen heterocyclic compounds of the invention include (1) derived resinous copolymers consisting essentially of not less than 25% by weight of polymerized units of the general structure:

(II)(a)



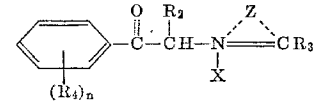
the remainder of the polymer molecule being polymerized units of the general structure:

(b)



and (2) non-polymeric compounds having the general structure:

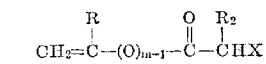
(III)



wherein R_2, R_3 X and Z are as previously defined; n and m each represents an integer of from 1 to 2; R_4 represents the hydrogen atom, an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl, pentadecyl, benzyl, phenethyl, etc.), a hydroxyl group, a halogen (e.g., chlorine or bromine), or an aryl group (e.g. phenyl, tolyl, biphenyl, etc.); and R represents the hydrogen atom, a lower alkyl group (e.g., methyl, ethyl, etc.), or an aryl group (e.g., phenyl, tolyl, etc.), etc., and wherein the said m, R, R_2 and X stand in each occurrence for the same defined member. The components of Formula II above are so chosen as to give compounds having molecular weights in each instance of at least 300.

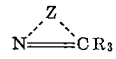
In accordance with the invention, we prepare the derived resinous copolymer coming under above Formula II by reacting a resinous addition polymer of a monoethylenically unsaturated polymerizable compound having the general formula:

(IV)



with a heterocyclic tertiary amine having the general formula:

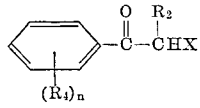
(V)



wherein *m*, R, R_2, R_3, X and Z are as defined above, under conditions that result in the desired degree of conversion of units of above Formula IV to the corresponding quaternary salts units represented by Formula II(*a*) above. The preferred starting polymers in the above process are polyvinyl chloroacetate described by Wiley et al., J. Poly, Sci., 3, 708 (1948) or copolymers containing vinyl chloroacetate and vinyl alcohol units prepared by partial esterification of polyvinyl alcohol with chloroacetic anhydride, and poly(vinyl chloromethyl ketone) prepared, for example, by polymerizing monomeric vinyl chloromethyl ketone (Cath et al., J. Chem. Soc., 1948, p. 278) in a solvent such as dioxane at 60° C. in the presence of a polymerization catalyst, e.g., azo-bis-isobutyronitrile. The proportions of the heterocyclic tertiary amine of Formula V above can vary widely, but preferably it is employed in the reaction in excess of the stoichiometrically calculated quantity, for example, from about 1.2 to 5, or more equivalent moles. Advantageously, the reaction is carried out in an inert reaction medium which is a solvent for the starting polymer such as, for example, in acetone, dimethyl sulfoxide, N,N-dimethylformamide, γ-butyrolactone, etc. The reaction mixture is allowed to stand for several days or more, at room temperatures or heated for several hours. The quaternary salt product which forms is isolated by precipitation into a nonsolvent for salt product, or in the case where the salt product forms as a precipitate in the reaction mixture, the supernatant liquor can be simply decanted. The quaternary salt product can then be further purified by washing with a nonsolvent and dried preferably under vacuum. The quaternary salt products consisting from about 25–100% by weight of quaternized units and from 75–0% by weight of unquaternized residual units have been found to be especially efficacious mordants in photographic layers and are preferred.

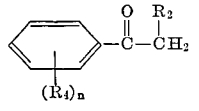
To prepare the nonpolymeric compounds of the invention coming under Formula III above, a compound having the general formula:

(VI)



wherein *n*, R_2, R_4 and X are as previously defined, is reacted with a tertiary heterocyclic amine of Formula V above, in approximately equimolar proportions, and the friable product obtained is crushed under ether, washed with ether and collected on a filter and dried. Alternatively, Formula III compounds can be prepared by reacting a compound having the general formula:

(VII)



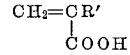
wherein *n*, R_2 and R_4 are as previously defined, with a mixture of a tertiary amine of Formula V above and a halogen such as chlorine, bromine, or iodine, preferably in about the molar ratios of 1:1:1 of the compounds of Formula VII, Formula V and halogen, respectively. Advantageously, the reaction mixture is heated for one or more hours, cooled and the solid product which forms is filtered off, washed with a nonsolvent, (e.g. acetone) and recrystallized from methanol.

As previously mentioned, the above defined polymeric mordants of the invention function as "alkali-release" modants. Thus, under appropriate conditions of pH, they decompose or rearrange to form betaines so as to lose

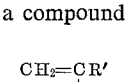
their ability to act as a mordant with release and subsequent removal of the mordanted dye from the system. Thus, for example, the bulky quaternary nitrogen compound which under acid or neutral conditions is capable of salt formation with an acidic dye may under alkaline conditions release the dye by decomposition of the mordant to separate the quaternary nitrogen fragment from the bulky residue or by a rearrangement reaction to produce a zwitterion with resultant internal charge compensation or by the loss of the quaternary nature of the nitrogen. A major advantage of the above "alkali release" mordants is, therefore, that the compounds do not retain either the previously mordanted dye or thiosulfate ion from the fixing bath after processing, as do other compounds of similar mordanting ability providing a neutral or mildly alkaline hypo bath is used.

The photographic elements prepared with the above-described polymeric and non-polymeric mordants of the invention comprise a support material having thereon at least one hydrophilic colloid layer containing a mordant of the invention, which layer may also contain a light-sensitive silver halide. However, the preferred light-sensitive photographic elements comprise a support having thereon at least one hydrophilic colloid layer containing a mordant of the invention and at least one light-sensitive silver halide emulsion layer. The mordant containing light-screening and antihalation layers are customarily prepared by coating on the support or photographic element by methods well known in the art, a water solution comprising at least one mordant of the invention, an acid dye, a water-permeable hydrophilic colloid binder and a coating aid such as saponin. For most purposes, it is also desirable to add agents to harden the colloidal binder material so that the light-screening layer will remain intact in the photographic element during and following the processing operations. The pH of the coating solution is adjusted when necessary to a level that is compatible with the light-sensitive emulsion layer by the usual methods. The proportions of mordant, dye, colloidal binder, hardener and coating aid may be varied over wide ranges and will depend upon the specific requirements of the photographic element being produced. The methods used to determine the optimum compositions are well known in the art and require no further elucidation here. Suitable support materials include any of those used in photography such as cellulose acetate, cellulose propionate, cellulose acetate-butyrate, cellulose nitrate, synthetic resins such as nylon, polyesters, polystyrene, polypropylene, etc., paper, and the like.

Suitable hydrophilic colloid materials that can be used in the mordant containing compositions and layers, and photographic elements, of the invention include gelatin, albumin, collodion, gum arabic, agar-agar, cellulose derivatives such as alkyl esters of carboxylated cellulose, hydroxy ethyl cellulose, carboxy methyl hydroxy ethyl cellulose, synthetic resins, such as the amphoteric copolymers described by Clavier et al. in U.S. Pat. 2,949,442, issued Aug. 16, 1960, polyvinyl alcohol, polyvinyl pyrrolidone, and others well known in the art. The above-mentioned amphoteric copolymers are made by polymerizing the monomer having the formula:



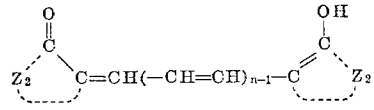
wherein R′ represents an atom of hydrogen or a methyl group, and a salt of a compound having the general formula:



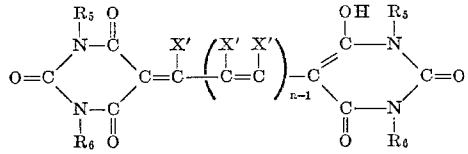
wherein R′ has the above-mentioned meaning, such as an alkylamine salt. These monomers can further be polymerized with a third unsaturated monomer in an amount up to about 20 percent, and preferably from 5–15 percent, of the total weight of monomer used, such as

an ethylene monomer that is copolymerizable with the two principal monomers. The third monomer may contain either a basic group or an acid group and may, for example, be vinyl acetate, vinyl chloride, acrylonitrile, methacrylonitrile, styrene, acrylates, methacrylates, acrylamide, methacrylamide, etc. Examples of these polymeric gelatin substitutes are copolymers of allylamine and methacrylic acid; copolymers of allylamine, acrylic acid and acrylamide; hydrolyzed copolymers of allylamine, methacrylic acid and vinyl acetate; the copolymers of allylamine, acrylic acid and styrene; the copolymers of allylamine, methacrylic acid and acrylonitrile; etc.

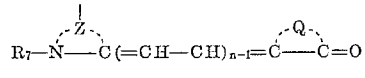
The dyes that can be effectively mordanted in accordance with our invention include any filter dye that has one or more acidic group substituents such as sulfo or carboxyl groups, for example, the oxonol dyes described and claimed in copending application of Joseph Bailey, Ser. No. 98,709, filed Mar. 27, 1961, 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 1 to 2 carbon atoms, R_6 is an alkyl group of from 1 to 8 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 1 to 4 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, having the formula:



wherein R_7 represents an alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, etc., or a carboxy-alkyl 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 sulfo-substituent 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 sulfo-substituted 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 formulas 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. 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-pyrazolin-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-pyrazolin - 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 - pyrazolone-(4)]pentamethineoxonol, and typical ultraviolet absorbing dyes include the 2,5-bis(substituted sulfophenyl)thiazolo[5,4-d] thiazole disodium salts of Sawdey U.S. Ser. 183,417, filed Mar. 29, 1962, such as 2,5-bis(o-methoxy-x-sulfophenyl)thiazolo[5,4-d]thiazole disodium salt, 2,5-bis(o-hexyloxy-x-sulfophenyl)thiazolo[5,4-d]thiazole disodium salt, 2,5-bis(o-decyloxy-x-sulfophenyl)thiazolo[5,4-d]thiazole disodium salt, 2,5-bis(o-methyl-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. 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-phenylimino-5-[3-(3-sulfobenzamido)benzal]-4-thiazolidone (sodium salt), 3-benzyl-2-phenylimino-5-o-sulfobenzal-4-thiazolidone (sodium salt), 5-(2,4-dicarboxymethoxybenzal) - 3 - phenyl - 2 - phenylimino-4-thiazolidone sodium salt, etc., tartrazine, and the like filter dyes.

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-diphenylbicyclo (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. Pats. 2,725,294 and 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. 2,725,305, issued Nov. 29, 1955; a bisester of methane-sulfonic acid such as 1,2-di(methanesulfonoxy)ethane as described in Allen and Laakso U.S. Pat. 2,726,162, issued Dec. 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak, U.S. Pat. 2,732,316, issued Jan. 24, 1956; a dialdehyde or a sodium bisulfite derivative thereof, the aldehyde groups of which are separated by 2–3 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. 2,950,197, issued Aug. 23, 1960; or 2,3-dihydroxydioxane as described in Jeffreys U.S. Pat. 2,870,013, issued Jan. 20, 1959.

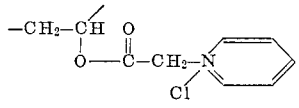
The photographic element utilizing our light-screening layers have light-sensitive emulsion layers containing silver chloride, silver bromide, silver chlorobromide, silver iodide, silver bromoiodide, silver chlorobromoiodide, etc., as the light-sensitive material. Any light-sensitive silver halide emulsion layers may be used in these photographic elements. The silver halide emulsion may be sensitized by any of the sensitizers commonly used to produce the desired sensitometric characteristics.

Our invention is further illustrated by the following examples describing the preparation of preferred mordants and the use thereof in photographic elements.

EXAMPLE 1

Poly(vinyl pyridinium acetate) chloride

(A) 20 g. (approx. 0.17 mol.) of polyvinyl chloroacetate was dissolved in 200 ml. of acetone. Then 40 ml. (approx. 0.47 mol.) of pyridine was added and the mixture allowed to stand overnight at room temperature. Soft material had precipitated. The supernatant liquid was decanted. The residue was dissolved in methanol, precipitated in ether, washed, and vacuum dried. It was then redissolved in methanol and reprecipitated in ether, washed, and vacuum dried. Analysis of this product showed that it contained 2.8% by weight of nitrogen as compared with calculated theory of approximately 7% by weight of nitrogen for pure poly(vinyl pyridinium acetate) chloride. Accordingly, this derived polymer consisted essentially of about 40% by weight of recurring (vinyl pyridinium acetate) chloride units of the structure:

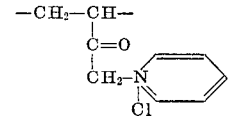


and the remainder of the polymer to make 100% of recurring units of unreacted vinyl chloroacetate.

(B) A solution of 6.0 g. (approx. 0.5 mol) of polyvinyl chloroacetate in 100 ml. of dimethyl sulfoxide was treated with 10 g. (approx. 0.13 mol.) of pyridine. The mixture was allowed to stand 5 days. The polymer was then precipitated in acetone, washed and vacuum dried. It was redissolved in methanol and reprecipitated in ether, washed and vacuum dried. The yield of product was 9 g. Analysis of this product showed that it contained 5.4% by weight of nitrogen and 13.8% by weight of chlorine as compared with calculated theory of approximately 7% by weight of nitrogen and 17.8% by weight of chlorine in essentially pure poly(vinyl pyridinium acetate) chloride. Accordingly, this derived polymer consisted essentially of about 77% by weight of recurring units of (vinyl pyridinium acetate) chloride and 23% by weight of recurring units of unreacted vinyl chloroacetate.

EXAMPLE 2

A solution of 60.0 g. (approx. 0.57 mol.) of poly(vinyl chloromethyl ketone) in 600 ml. of N,N-dimethylformamide was treated with 125 ml. (approx. 1.58 mol.) of pyridine. The mixture was allowed to stand for 6 days. A soft precipitate formed. The supernatant liquor gave no precipitate in ether and discarded. The residue was dissolved in 150 ml. of methanol, precipitated in acetone, washed and vacuum dried. It was redissolved in methanol, reprecipitated in acetone and dried. The yield was 55 g. Analysis of this product showed that it contained 3.8% by weight of nitrogen as compared with calculated theory of approximately 7.6% by weight of nitrogen. Accordingly, this derived polymer consisted essentially of about 49.8% by weight of recurring (vinyl pyridinium methyl ketone) chloride units of the structure:



and the remainder of the polymer molecule to make 100% of recurring units of unreacted vinyl chloromethyl ketone.

The use of our "alkali-release" polymers as mordants in filter layers will be illustrated with the following examples.

EXAMPLE 3

To 10 cc. of 10% photographic gelatin melted at 40° C. was added 30 mg. of poly(vinyl pyridinium acetate) chloride dissolved in 10 cc. of water. The pH of the solution was adjusted to 4.5–5.0 with glacial acetic acid. To this was added 10 mgs. of bis[3-methyl-1-p-sulfophenyl - 5 - pyrazolone(4)]pentamethineoxonol dissolved in water with vigorous stirring. The pH of the melt was then readjusted to 6.0±0.1 with 2.5 N sodium hydroxide solution, a coating aid added, the total volume adjusted to 32 cc. with distilled water and the melt coated on a film support and dried.

No signs of dye bleeding out of the gel layer were noted when a portion of the dried coating was immersed in stagnant distilled water at 75° F. for 2 minutes, nor after a second 2-minute immersion in the water.

Another portion of the coating was treated in a conventional alkaline silver halide developer solution containing hydroquinone and n-methylaminophenol sulfate as the developing agents. The mordanted dye was completely bleached by this treatment. Following treatment in the developer, the coating was treated in a conventional sodium thiosulfate fixing bath and then washed. No residual sodium thiosulfate was detected in the coating by the Ross-Crabtree method.

Similar results were obtained when coatings were made substituting the corresponding trimethineoxonol dye and the corresponding monomethine oxonol dye for the pentamethineoxonol dye. Coatings were made in which each of the above dyes were mordanted with poly(vinyl pyridinium methyl ketone) chloride instead of poly(vinyl pyridinium acetate) chloride. Each of these coatings showed no bleeding of dyes on immersion in water, but complete dye bleaching in the developer solution. No residual sodium thiosulfate was detected by the Ross-Crabtree method in the developed, fixed and washed coatings.

EXAMPLE 4

This example shows the use of the derived polymers of the invention as an ultraviolet absorbing overcoating layer over light-sensitive gelatino-silver halide emulsion layers, for example, over the emulsion layers of a multilayer color element of the type described in Mannes et al., U.S. Pat. 2,252,718, issued Aug. 19, 1941.

A gelatin-mordant composition was prepared by mixing 200 g. of a 10% aqueous gelatin solution at 40° C. and 200 g. of a 15% aqueous solution of the polymeric mordant prepared according to Example 1A at 40° C. The clear solution obtained was then chilled, noodled, and washed with cold water in the normal manner for 6 hours, drained, remelted at 50° C. and weighed.

A coating melt was then prepared as follows employing the above gelatin-mordant composition.

Coating melt

Gelatin containing 7.7 g. of Example 1 polymer—188 g.
Melt at 40° C. and then added premixed:
10% solution in water of the dye 2,5-bis(2-methoxy-x-sulfophenyl)thiazolo[5,4-d] - thiazole disodium salt—25.5 cc.
20% triton NE (an organic polyether alcohol)—1 cc.
Distilled water—125 cc.
Then add successively from aqueous solution:
Mucochloric acid—15.6 mg.
Diacetyl—12.3 mg.
Sulfur dioxide hydroquinone clathrate—0.32 g.
Adjust solution pH=6.07±0.07 with lauric acid
Adjust solution pH=6.2
Distilled water (to make total melt)—383 g.

The sulfur dioxide hydroquinone clathrate is described by H. M. Powell, J. Chem. Soc. (1948), pages 61–73; C. A. 42, 5293 (1948). This melt was then coated over the emulsion layers of the above-mentioned multilayer color element at 6 g./sq. ft. (containing 1.33% gelatin) to give a coating comprising 120 mg./sq. ft. of the polymeric mordant of Example 1 and 40 mg./sq. ft. of the filter dye in 80 mg./sq. ft. of gel. On sectioning of the coated element and in photographs made therewith, no bleeding of the dye was noted. Alkaline processing conditions left no dye residue and yet no stain increase was noted, implying betaine formation of the mordant with internal charge compensation. Also, no detectable thiosulfate was retained in the fixed element.

Our alkali-release polymeric mordants are also used to advantage in mordanting light-filtering dyes, such as a blue-light absorbing dye having one or more acid substituents, in a filtering layer between the top blue-sensitive layer and over the green-sensitive and the red-sensitive layers of a multilayer color photographic element of the type described in Mannes et al. U.S. Pat. 2,252,718, referred to previously. Alternatively, appropriate dyes of other colors can be used to advantage in mordanted filter layers between the green-sensitive and red-sensitive layers, or one or more appropriate dyes can be mordanted in an antihalation layer either between the lightsensitive layers and the support or on the side of the support away from the light-sensitive layers.

Examples 5 through 8 illustrate the use of the derived polymeric mordants of the invention in antihalation layers, and further illustrate the improvement obtained therewith in regard to hypo retention in the processed elements, as compared with an element prepared with a known mordanting polymer and a non-mordanted control element.

In each of the following examples, the coating melts were prepared, in general, by the procedure described in above Example 4. The melt compositions, with the exception of the control example, were coated on an ordinary cellulose acetate film support and over this melt layer was coated in each case a fine-grained silver chlorobromide gelatin emulsion layer. For convenience, the filter dyes employed are listed as follows:

Dye A—4-[(3-ethyl-2(3H)-benzoxazolylidene)ethylidene]-3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one, monosulfonated
Dye B—Bis(1-butyl-3-carboxymethyl-5-barbituric acid) trimethineoxonol
Dye C—4-[4-(3-ethyl-2(3H)-benzoxazolylidene)-2-butenylidene]-3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one, monsulfonated
Dye D—Bis(1-butyl-3-carboxymethyl-5-barbituric acid) pentamethineoxonol
Dye E—Bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)]methineoxonol
Dye F—Bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)]-trimethineoxonol

Dye G—Bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one(4)]-pentamethineoxonol

EXAMPLE 5

A control film element was coated having no antihalation undercoat.

EXAMPLE 6

A film element was coated having an antihalation undercoat comprising gelatin+poly(α - methylallyl - N-guanidyl-ketimine, glylcolic acid salt) prepared in accordance with Minsk U.S. Pat. 2,882,156, issued Apr. 14, 1959, as the mordant polymer (28 mg./ft.^{2}), Dye A (2.4 mg./ft.^{2}), Dye B (1.6 mg./ft.^{2}), Dye C (2.9 mg./ft.^{2}) and Dye D (2.5 mg./ft.^{2})

EXAMPLE 7

A film element was coated having an antihalation undercoat comprising gelatin and the polymeric mordant of Example 1A (45 mg./ft.^{2}), Dye A (2.4 mg./ft.^{2}), Dye B (1.6 mg./ft.^{2}), Dye C (2.9 mg./ft.^{2}) and Dye D (2.5 mg./ft.^{2}).

EXAMPLE 8

A film element was coated having an antihalation undercoat comprising gelatin and the polymeric mordant of Example 1A (45 mg./ft.^{2}), Dye E (5 mg./ft.^{2}), Dye F (5 mg./ft.^{2}) and Dye G (5 mg./ft.^{2}).

The film coatings of above Examples 5, 6, 7 and 8 were exposed on an intensity scale sensitometer, developed for 2′ in a conventional alkaline developer solution using hydroquinone and p-methylaminophenol sulfate as the developing agents at 80° F., fixed in a conventional sodium thiosulfate fixing bath that was substantially neutral, washed and dried. The processed strips were analyzed for residual hypo. The following results were obtained:

	Relative speed	γ	Fog	Hypo retention (mg./in.^{2})
Example:				
5	105	2.08	.02	.001
6	100	1.96	.01	.032
7	162	2.24	.16	.009
8	107	2.16	.02	.002

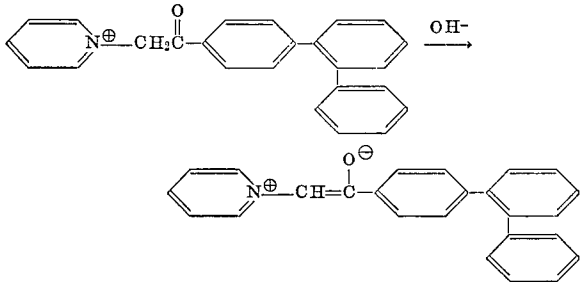
It will be noted from the above-tabulated results that the hypo retention by the film elements prepared with a polymeric mordant of the invention (Examples 7 and 8) was practically negligible in amount ranging only from 0.002 to 0.009 mg./in.^{2}, whereas the film element (Example 6) prepared with poly [α-methylallyl-N-guanidyl-ketimine, glycolic acid salt] showed a hypo retention many fold greater of 0.032 mg./in.^{2}.

EXAMPLE 9

1-(4-o-biphenylylphenacyl)pyridinium iodide

4-acetyl-o-terphenyl (1 mol., 13.6 g.) was placed in a 300 ml. three-necked flask fitted with a reflux condenser and mechanical stirrer, dry pyridine (25 ml.) was added with stirring, then iodine (1 mol., 13 g.) was added and a small amount of heat was evolved. At this point a tube containing a desiccant was placed in the end of the condenser to keep the system dry. The mixture was then heated on a steam bath with good stirring for two hours, cooled, solid product filtered off, washed on a Buchner funnel with an excess of acetone and dried. After two recrystallizations from methyl alcohol the yield of yellow solid was 13 g. (54%), M.P. 250–251° C. with decomposition.

This compound forms the yellow betaine upon treatment with alkali with a resultant internal charge compensation as follows:



This compound, at a ratio of 5 parts by weight to 1 part by weight of dye, mordanted the dye bis[3-methyl-1-p-sulfophenyl - 5 - pyrazolone-(4)]-pentamethineoxonol in gelatin with no bleeding upon washing in water. The mordanted dye was bleached in a developer having the composition:

	G.
p-Methylaminophenol sulfate	4.5
Sodium sulfite, desiccated	90.0
Hydroquinone	8.0
Sodium carbonate, monohydrated	52.5
Potassium bromide	5.0
Water to make 1.0 liter	

with the yellow betaine color remaining; the bleaching was increased when the alkalinity of the developer was increased by the addition of sodium hydroxide. This yellow color was discharged by subsequent acidification of the gelatin coating. Although this mordant prevented bleeding of the dye in water, washing of the gelatin layer in dilute alkali resulted in substantially complete washing out of the dye.

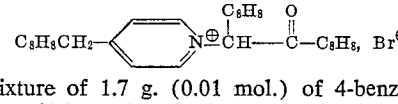
In the place of the specified mordant in the above example, there can be substituted an equivalent amount of related mordanting compounds including the following:

1-(4-o-biphenylylphenacyl)pyridinium bromide
1-(4-o-biphenylyl)phenacyl-3-methylimidazolium iodide
1-(4-o-biphenylyl)phenacyl-3-methylbenzimidazolium iodide
1-(4-o-biphenylyl)phenacyl-3-ethyl-naphtho[2,3-d]-imidazolium iodide
1-(4-o-biphenylyl)phenacyl-4-methyltetrazolium bromide
1-(4-o-biphenylyl)phenacyl-4-phenyltetrazolium bromide
1-(4-o-biphenylyl)phenacyl-4-methylthiazolium bromide
1-(4-o-biphenylyl)phenacyl-4-phenylthiazolium bromide
1-(4-o-biphenylyl)phenacyl-3-methylquinolium iodide
1-(4-o-biphenylyl)phenacyl-4-methylisoquinolium iodide.

These compounds likewise function effectively as alkali-release mordants in the photographic use process described above, and can be prepared, in general, by the described procedure by substituting therein the appropriate intermediates.

EXAMPLE 10

4-benzyl-1-(2-phenylphenacyl)pyridinium bromide



A mixture of 1.7 g. (0.01 mol.) of 4-benzylpyridine and 2.7 g. (0.01 mol.) of 2-bromo-2-phenylacetophenone was heated on the hot plate until the reaction became exothermic. The product was a glass which was chipped out and crushed under ether, washed with ether and collected on a filter and dried. The yield was 4.4 g. of product analyzing $C_{26}H_{22}NOBr$. This compound was tested in the following manner:

Melt A—7.5% aqueous gelatin solution, pH 6.0
Melt B—2.96 ml. of a 33.8% solution of bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one - (4)] methineoxonol, 11.83 ml. of a 8.45% solution of bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)] trimethineoxonol, 5.91 ml. of a 16.9% solution of bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)] pentamethineoxonol and distilled water to make up to 300 ml.
Melt C—90 mg. of above mordant in 3 ml. of distilled water (methanol may also be used if necessary for solution)

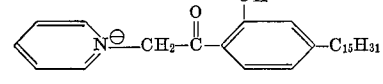
To 12 ml. of melt A was added 0.3 ml. of a 15.34% solution of saponin; then melt C was added with mechanical agitation at 40° C. Then 3.0 ml. of melt 13 was added slowly with mechanical agitation. This final melt was then coated on a cellulose acetate film support on a hand-coated block at 104° F., chill-set and dried at room temperature. Small pieces of the coatings were tested for dye bleeding in water and for bleaching in the aforementioned developer, followed by treating in a fixing bath of the following composition:

Sodium thiosulfate—240.0 g.
Sodium sulfite, desiccated—15.0 g.
Acetic acid 28%—48 cc.
Boric acid, crystals—7.5 g.
Potassium alum—15.0 g.
Water to make 1.0 liter.

Result: Mordanted well. Bleached slowly in the developer. Retained no hypo.

EXAMPLE 11

1-(2'-hydroxy-4'-pentadecylphenacyl)pyridinium iodide



This compound was prepared by the procedure of above Example 10, except that the reactants were pyridine and 2-hydroxy-4-pentadecylphenacyl iodide. On testing this compound in accordance with the method described in Example 10, it was found to mordant well, to bleach rapidly and to retain no hypo in the aforementioned developer and fixing compositions.

Other compounds of the invention coming under Formula III above that were found to have excellent mordanting properties and to function as good alkali-release materials include:

4-benzyl-1-phenacylpyridinium bromide
2-phenacylisoquinolinium bromide
1-phenacylquinolinium bromide
4-benzyl-1-(2-methylphenacyl)pyridinium bromide
1-(α-phenylphenacyl)pyridinium iodide
4-diphenylmethyl-1-phenacylpyridinium bromide
4-diphenylmethyl-1-(α-phenylphenacyl)pyridinium iodide
3-diphenylmethyl-1-phenacylpyridinium iodide
3-diphenylmethyl-1-(α-phenylphenacyl)pyridinium bromide
4-(hydroxydiphenylmethyl)-1-phenacylpyridinium bromide
4-(hydroxydiphenylmethyl)-1-(α-phenylphenacyl)-pyridinium bromide
3,5-di-n-butyl-1-phenacylpyridinium bromide
3,5-di-n-butyl-1-(α-phenylphenacyl)pyridinium bromide
5-ethyl-1-phenacyl-2-picolinium bromide

The above list of compounds can be prepared in accordance with the procedures set forth hereinabove.

In the accompanying drawing which further illustrates the preferred photographic elements of our invention:

FIG. 1 shows light-screening layer **10** comprising gelatin, an acid substituted filter dye and the polymeric mordant of Example 1A, poly(vinyl pyridinium acetate) chloride, coated over a light-sensitive silver halide emulsion layer **11** which is coated on support **12**.

FIG. 2 shows antihalation layer **15** comprising gelatin, an acid substituted dye and the polymeric mordant of

Example 1A, poly(vinyl pyridinium acetate) chloride, coated adjacent to support **16** and a light-sensitive silver halide emulsion layer **14** coated over layer **15**.

FIG. 3 shows a multilayer color element comprising a support **21** having a red-sensitive silver halide emulsion layer **20** coated thereon, a green-sensitive silver halide emulsion layer **19** coated over layer **20**, a light-screening layer **18** comprising gelatin, an acid substituted dye, and the polymer mordant of Example 1A, poly(vinyl pyridinium acetate) chloride, coated over layer **19**, and a blue-sensitive silver halide emulsion layer **17** coated over layer **18**.

Similar results are obtained by substituting the following mordants for poly(vinyl pyridiniumacetate chloride) in the preceding examples:

poly(vinyl pyridinium-α-methylacetate chloride)
poly(vinyl pyridinium-α-phenylacetate chloride)
poly(vinyl 2-methylthiazoliumacetate chloride)
poly(vinyl 2-ethylselenazoliumacetate chloride)
poly(vinyl quinoliniumacetate chloride)
poly(vinyl 1,2-dimethylimidazoliumacetate chloride)
poly(vinyl 5-methyl-1,2,3,4-tetrazoliumacetate chloride)
poly(vinyl pyridiniummethyl ketone chloride)
poly(vinyl 2-methylthiazoliummethyl ketone chloride)
poly(vinyl 2-phenylbenzoxazoliummethyl ketone chloride)
poly(vinyl quinoliniummethyl ketone chloride)

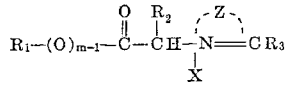
The above mordants are prepared according to the methods of the inventions described in Examples 1 and 2 by reacting polyvinyl chloroacetate or poly(vinyl chloromethyl ketone) with the appropriate heterocyclic amine.

The use of our alkali-release mordants in light-screening layers over light-sensitive silver halide emulsion layers, and in antihalation undercoat layers, to produce improved photographic elements has been illustrated in the preceding examples. However, it will be apparent that the mordants of the invention can also be advantageously used in light-screening layers between two or more color sensitized silver halide emulsion layers, or in antihalation backing layers, or incorporated directly in light-sensitive silver halide emulsion layers, or they can be used to prepare imbibition dye transfer blanks of improved properties.

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 as described hereinabove and as defined in the appended claims.

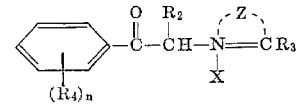
We claim:

1. A compound which functions as an alkali-release mordant for acid dyes, said compound represented by the formula:



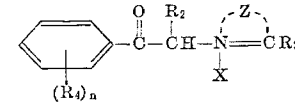
wherein *m* represents an integer of from 1 to 2; R_1 represents a member selected from the class consisting of alkyl having from 1 to 18 carbon atoms, phenyl, alkylphenyl in which the alkyl group has from 1 to 15 carbon atoms, hydroxyphenyl, halophenyl, phenylmethylphenyl, phenylethylphenyl, diphenyl, methyldiphenyl, terphenyl and naphthyl; R_2 represents a member selected from the class consisting of hydrogen, lower alkyl and phenyl group; R_3 represents a member selected from the class consisting of hydrogen, alkyl having from 1 to 15 carbon atoms and a phenyl group; X represents an anion selected from the class consisting of bromide, iodide, chloride, thiocyanate, sulfamate, perchlorate, lower alkyl sulfate and p-toluenesulfonate; and Z represents the nonmetallic atoms required to complete a pyridine nucleus.

2. A compound which functions as an alkali-release mordant for acid dyes, said compound represented by the formula:



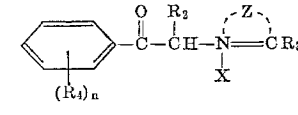
wherein *n* represents an integer of from 1 to 2; R_2 represents a member selected from the class consisting of hydrogen, lower alkyl phenyl, tolyl or biphenylyl groups; R_3 represents a member selected from the class consisting of hydrogen, alkyl having from 1 to 15 carbon atoms phenyl, tolyl or biphenylyl groups; R_4 represents a member selected from the class consisting of hydrogen, hydroxyl, an alkyl group having from 1 to 15 carbon atoms phenyl, tolyl or biphenylyl groups; X represents an anion selected from the class consisting of bromide, iodide, chloride, thiocyanate, sulfamate, perchlorate, lower alkyl sulfate and p-toluenesulfonate; Z represents the nonmetallic atoms required to complete a pyridine nucleus.

3. A compound which functions as an alkali-release mordant for acid dyes, said compound represented by the formula:



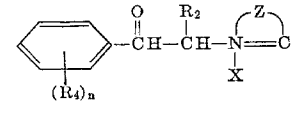
wherein *n* represents an integer of from 1 to 2; R_2 represents a member selected from the class consisting of hydrogen and phenyl; R_3 represents a member selected from the class consisting of hydrogen, lower alkyl, benzyl and phenyl; R_4 represents a member selected from the class consisting of hydrogen, hydroxyl, alkyl of from 1 to 15 carbon atoms, phenyl and diphenyl; X represents an anion selected from the class consisting of bromide, iodide, chloride, thiocyanate, sulfamate, perchlorate, lower alkylsulfate and p-toluenesulfonate; and Z represents the nonmetallic atoms required to complete a pyridine nucleus.

4. A compound which functions as an alkali-release mordant for acid dyes, said compound being represented by the formula:



wherein *n* represents an integer of from 1 to 2; R_2 represents a member selected from the class consisting of hydrogen and phenyl; R_3 represents a member selected from the class consisting of hydrogen, methyl, ethyl, benzyl, and phenyl; R_4 represents a member selected from the class consisting of hydrogen, hydroxyl, pentadecyl and diphenyl; X represents an anion selected from the class consisting of bromide, iodide, chloride, thiocyanate, sulfamate, perchlorate, lower alkylsulfate and p-toluenesulfonate; and Z represents the nonmetallic atoms required to complete a pyridine nucleus.

5. A compound which functions as an alkali-release mordant for acid dyes, said compound being represented by the formula:



wherein *n* represents an integer of from 1 to 2; R_2 represents a member selected from the class consisting of hydrogen and phenyl; R_3 represents a member selected from the class consisting of hydrogen and benzyl; R_4

represents a member selected from the class consisting of hydrogen, hydroxyl, diphenyl and pentadecyl; X represents an anion selected from the class consisting of bromide and iodide; and Z represents the nonmetallic atoms required to complete a pyridine nucleus.

6. The compound 1 - (4 - o - biphenylylphenacyl) pyridinium iodide.

7. The compound 4 - benzyl - 1-(2 - phenylphenacyl) pyridinium bromide.

8. The compound 1 - (2' - hydroxy - 4' - pentadecylphenacyl)pyridinium iodide.

References Cited

UNITED STATES PATENTS

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3,489,759	6/1970	Fields et al.	260—295

ALAN L. ROTMAN, Primary Examiner

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96—57, 84; 117—33.3; 260—289, 286, 294.8, 298, 302, 304, 306.7, 307, 308, 309, 309.2, 326.11