Feb. 4, 1969 R. C. TABER ET AL 3,425,833

MORDANTS FOR BLEACHABLE FILTER LAYERS

Filed Aug. 16, 1965

FIG. 1

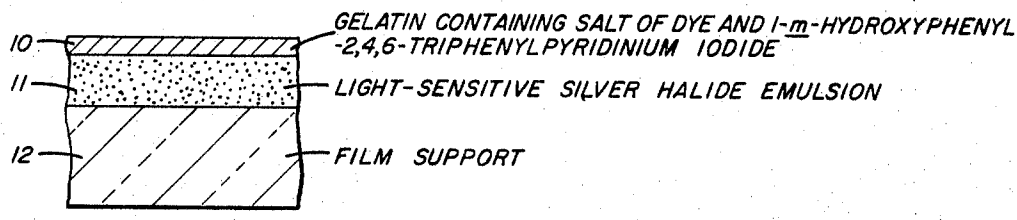


FIG. 2

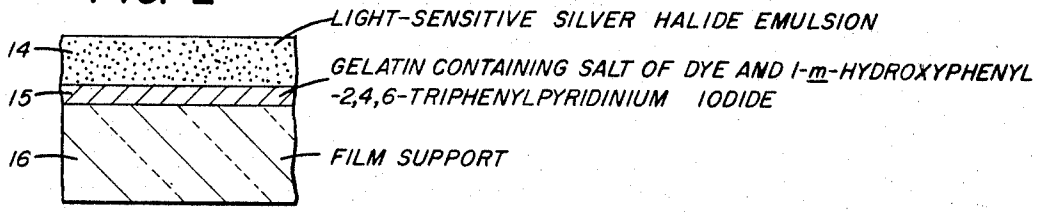
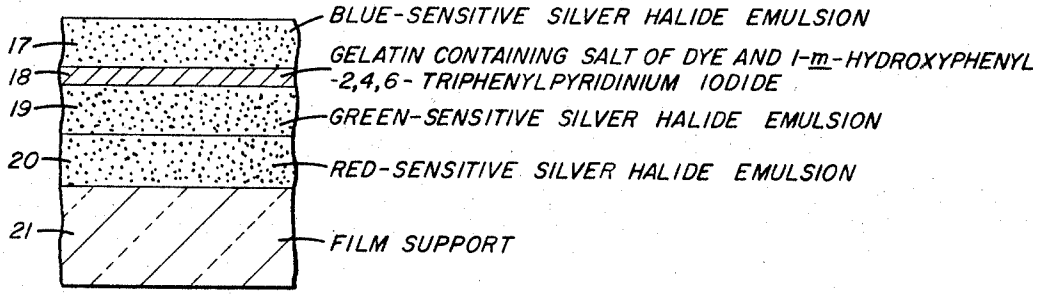


FIG. 3



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MORDANTS FOR BLEACHABLE FILTER LAYERS

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Int. Cl. G03c 1/84

This invention relates to certain bulky, i.e., relatively high molecular weight, quaternary nitrogen heterocyclic compounds containing a phenolic group 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 is 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.

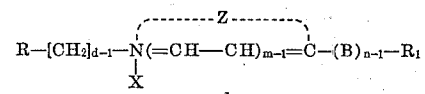
Numerous substances have been proposed as mordants to prepare the dye-mordant salts used as light-screening and light-absorbing materials for the purposes indicated above. Among the proposed mordants are relatively high molecular weight compounds having ionic charges opposite to those of the particular light-absorbing dye. For example, the dye employed might be an acid dye, in which case the mordant would be a cationic. 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. Patents 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 limitations, they have not been found entirely satisfactory in many applications primarily because these polymeric mordants on alkaline development and release of the dye, still retain their mordanting property and, accordingly, not only tend to retain some residual dye as evidences by background stain or coloration in the layers, 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 poor keeping stability of the produced images. 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 quaternary nitrogen heterocyclic compounds containing phenolic groups are especially useful as precipitants and mordants for acid dyes in photographic layers, and that these compounds satisfactorily overcome the above-mentioned shortcomings of heretofore known mordants for this purpose. Thus, when incorporated in photographic layers, they function effectively as "alkali-release" mordants without retention of any residual dye or deleterious amounts of thiosulfate ion in the layers on processing, and the produced images are of very good quality and of outstanding keeping properties. These mordants are soluble in aqueous solutions, for example, dilute solutions of acids such as acetic, butyric, lauric, etc. acids. Furthermore, they readily form substantially non-diffusable salts with water-soluble dyes, and these are all compatible with various hydrophilic materials such as gelatin. They are compounds of definite constitution and, in general, have molecular weights of about at least 300.

It is, accordingly, an object of the invention to provide a photographic element having one or more layers containing at least one of the bulky nitrogen heterocyclic compounds or salts of the invention described above. Another object is to provide a backing layer containing at least one of these salts. 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 an imbibition blank containing at least one of the above salts. 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 overcoating layers for photographic elements which contain at least one of the above salts. Another object is to provide a process for preparing the bulky quaternary nitrogen heterocyclic compounds and salts thereof. Other objects will become apparent from consideration of the description and the examples.

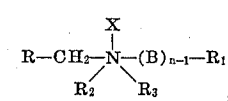
The phenolic group containing bulky quaternary heterocyclic compounds that are useful as "alkali-release" mordants include those represented by the following general formulas:

I.



and

II.



wherein *d*, *m* and *n* represent an integer of from 1 to 2, R represents the hydrogen atom, an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl,

etc.), an aryl group (e.g., phenyl, tolyl, naphthyl, a phenolic group or ring such as p-hydroxyphenyl, 4-hydroxy-3,5-dibromophenyl, 2 - hydroxy-5-octylphenyl, 5-hydroxynaphthyl, etc.), R_1 represents an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl, etc.), an aryl group (e.g., phenyl, tolyl, naphthyl, a phenolic group or ring such as p-hydroxyphenyl, 4-hydroxy-3,5-dibromophenyl, 2 - hydroxy-5-octylphenyl, 4-hydroxynaphthyl, etc.), R_2 and R_3 each represents an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl, etc.), an aryl group (e.g., phenyl, tolyl, naphthyl, etc.), or an aralkyl group (e.g., benzyl, phenethyl, etc.), R_2 and R_3 together represent a divalent straight or branched chain alkylene group having from 4 to 5 carbon atoms in the chain (e.g., tetramethylene, pentamethylene, 4-methylpentamethylene, etc.), X represents an acid anion (e.g., chloride, bromide, iodide, thiocyanate, sulfamate, perchlorate, methyl sulfate, ethyl sulfate, p-toluenesulfonate, etc.), B represents the group CH=CH, the group $(CH=CH)_2$, the group $(CH=CH)_3$, or the p-phenylene group, and Z represents the nonmetallic atoms required to complete a heterocyclic nucleus having from 5–6 members in the heterocyclic ring, such as a thiazole nucleus

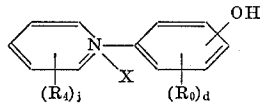
(e.g., thiazole,
4-methylthiazole,
4-phenylthiazole,
4'-p-hydroxyphenyl)-thiazole,
5-methylthiazole,
5-phenylthiazole,
5-(o-hydroxyphenyl)-thiazole,
4,5-dimethylthiazole,
4,5-diphenylthiazole,
4-(2-thienyl)thiazole, etc.),
a benzothiazole nucleus
(e.g., benzothiazole,
4-hydroxybenzothiazole,
4-chlorobenzothiazole,
5-chlorobenzothiazole,
6-chlorobenzothiazole,
7-chlorobenzothiazole,
4-methylbenzothiazole,
5-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 naphthothiazole nucleus
(e.g., α-naphthiazole,
β-naphthothiazole,
5-methoxy-β-naphthothiazole,
5-ethoxy-β-naphthothiazole,
7-methoxy-α-naphthothiazole,
8-methoxy-α-naphthothiazole,
5-hydroxy-β-naphthothiazole,
7-hydroxy-α-naphthothiazole, etc.),
a thianaphtheno-7',6',4,5-thiazole nucleus
(e.g., 4-methoxythianaphtheno-7',6',4,5-thiazole, etc.),
an oxazole nucleus
(e.g., 4-methyloxazole,
5-methyloxazole,
4-phenyloxazole,
4-(p-hydroxyphenyl)oxazole,
4,5-diphenyloxazole,
4-ethyloxazole,
4,5-dimethyloxazole,
5-phenyloxazole,
5-(m-hydroxyphenyl)oxazole, 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,
6-methoxybenzoxazole,
5-hydroxybenzoxazole,
6-hydroxybenzoxazole, etc.),
a naphthoxazole nucleus
(e.g., α-naphthoxazole,
β,β-naphthoxazole,
β-naphthoxazole,
6-hydroxy-β-naphthoxazole, etc.),
a selenazole nucleus
(e.g., 4-methylselenazole,
4-phenylselenazole,
4-(p-hydroxyphenyl) selenazole, etc.),
a benzoselenazole nucleus
(e.g., benzoselenazole,
5-chlorobenzoselenazole,
5-methoxybenzoselenazole,
5-hydroxybenzoselenazole,
tetrahydrobenzoselenazole, etc.),
a naphthoselenazole nucleus
(e.g., α-naphthoselenazole,
β,β-naphthoselenazole,
β-naphthoselenazole,
7-hydroxy-β-naphthoselenazole, etc.),
a thiazoline nucleus
(e.g., thiazoline,
4-methylthiazoline,
4-(p-hydroxyphenyl)thiazoline, 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,
5-hydroxy-3,3-dimethylindolenine,
3,3,5-trimethylindolenine,
3,3,7-trimethylindolenine, etc.),
a pyridine nucleus
(e.g., pyridine,
4-methylpyridine,
6-methylpyridine,
4,6-dimethylpyridine,
4-butylpyridine,
4-decylpyridine,
4-octadecylpyridine,

4,6-dibutylpyridine,
4-benzylpyridine,
6-benzylpyridine,
4-phenylpyridine,
4-(p-hydroxyphenyl)pyridine,
4,6-diphenylpyridine,
4,6-dinaphthylpyridine,
4-(2-thienyl)pyridine,
6-(2-thienyl)pyridine,
4,6-di(2-thienyl)pyridine,
4-(2-pyrryl)pyridine,
4-(2-indolyl)pyridine,
4-(3-indolyl)pyridine,
4-(3-pyridyl)pyridine,
4-(4-pyridyl)pyridine,
4,6-di(2-pyrryl)pyridine,
4-chloropyridine,
4-bromopyridine,
4,6-dichloropyridine,
4-chloro-6-bromopyridine,
4-phenoxypyridine,
4-alkoxypyridines,
6-alkoxypyridines,
4,6-dialkoxypyridine,
4-(2-furyl)pyridine, etc.),
an imidazole nucleus
(e.g., imidazole,
1-alkylimidazole,
1-alkyl-4-phenylimidazole,
4-(p-hydroxyphenyl)imidazole,
1-alkyl-4,5-dimethylimidazole, etc.),
a benzimidazole nucleus
(e.g., benzimidazole,
5-hydroxybenzimidazole,
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,
1-alkyl-6-hydroxy-β-naphthimidazole, etc.),
a thiadiazole nucleus
(e.g., 1,2,4-thiadiazole),
an oxadiazole nucleus
(e.g., 1,2,4-oxadiazole,
1,3,4-oxadiazole,
5-(p-hydroxyphenyl)-1,2,4-oxadiazole, etc.),
a 1 or 4 alkyl or aryl-1,2,4-triazole nucleus
(e.g., 1-methyl-1,2,4-triazole,
1-butyl-1,2,4-triazole,
5-(p-hydroxyphenyl)-1,2,4-triazole, etc.),
a tetrazole nucleus
(e.g., tetrazole,
5-butyl-1,2,3,4-tetrazole,
5-phenyl-1,2,3,4-tetrazole,
5-(o-hydroxyphenyl)-1,2,3,4-tetrazole, etc.),

and the like nuclei. The components of Formulas I and II are so chosen as to give compounds having molecular weights in each instance of at least 300. They are further chosen so that at least one of the members represented by R, R_1 and Z in each instance contains a phenolic group or ring. It will be understood that the term "phenolic" as used herein also includes fused phenolic rings.

More particularly, the phenolic group or residue containing bulky quaternary nitrogen heterocyclic compounds of the invention that are especially suitable as "alkali-release" mordants in photographic layers include those represented by the following general formula:

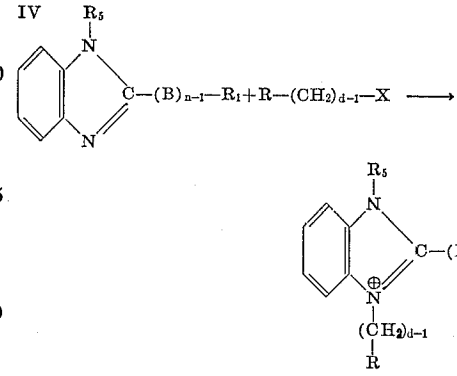
III.



j represents an integer of from 1 to 3, *d*, and X are as previously defined, R_4 and R_0 each represent a member, such as, the hydrogen atom, a halogen atom (e.g., chlorine or bromine), an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl, hexyl, dodecyl, octadecyl, benzyl, phenethyl, methoxymethyl, ethoxybutyl, isopropoxybutyl, butoxdodecyl, etc.), an aryl group (e.g., phenyl, hydroxyphenyl, tolyl, naphthyl, etc.), an alkoxy group (e.g., methoxy, ethoxy, butoxy, etc.), an aryloxy group (e.g., phenoxy, tolyloxy, naphthoxy, etc.), or a heterocyclic nucleus (e.g., 2-thienyl, 2-pyrryl, 2-indolyl, 3-indolyl, 2-furyl, 3-pyridyl, 4-pyridyl, etc.). The R_4 and R_0 components and the values of *d* and *j* in Formula III above are so chosen as to give compounds having molecular weights in each instance of at least 300.

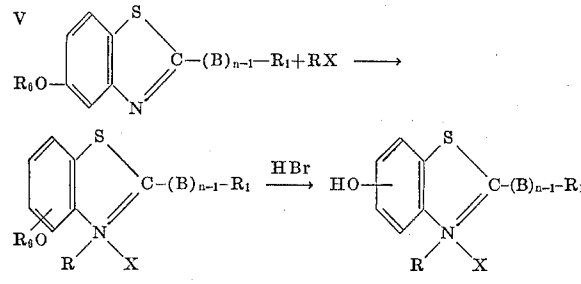
In accordance with the invention, we prepare the various salt compounds coming under Formula I above in a number of ways depending on the compounds to be prepared. For example, any of the pyridinium salts of Formula I can be readily prepared from the corresponding pyrylium salts by reaction with the appropriate aminophenol intermediates as described hereinafter. Salts of most other heterocyclic bases where the phenolic residue is in the group on the nitrogen atom have to be prepared, for example, as illustrated in the following reaction where the R group contains a phenolic residue such as previously defined

IV



and wherein *d*, *n*, B and X are as previously defined, and R_5 represents, for example, the hydrogen atom or an alkyl group. Those salts where the phenolic group is a substituent on the heterocyclic ring are conveniently prepared by a two step synthesis, for example, as illustrated in the following reaction:

V



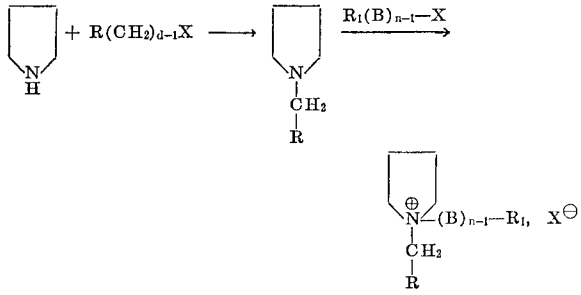
wherein *n*, B, R, R_1 and X are as previously defined, and R_6 represents an alkyl group.

In place of the starting heterocyclic compounds in above reaction Formulas IV and V, there may be substituted any other of the heterocyclic compounds completed by Z in Formula I such as thiazoles, benzothiazoles, naphthothiazoles, oxazoles, benzoxazoles, naphthoxazoles, selenazoles, benzoselenazoles, naphthoselenazoles, thiazolines, quinolines, indolenines, imidazoles, benzimidazoles, naphthimidizoles, thiadiazoles, oxadiazoles, triazoles, tetrazoles, etc., to give the corresponding compounds of the invention defined by Formula I above.

Salts of the pyrrolidone and piperidine compounds com-

ing under Formula II above also require a two step synthesis, for example, as illustrated in the following reaction:

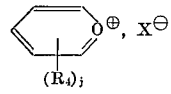
VI.



wherein R contains the phenolic residue such as defined previously, and *d*, *n*, R_1, and X are as previously defined. It will be understood that one or more of the carbon atoms of the heterocyclic compound can be substituted with appropriate substituents, e.g., alkyl groups such as methyl, ethyl, etc.

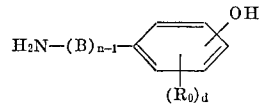
To prepare the preferred pyridinium compounds of the invention coming under Formula III above, a pyrylium salt of the formula:

VII.



wherein *j*, R_4 and X are as previously defined, is reacted with a compound of the formula:

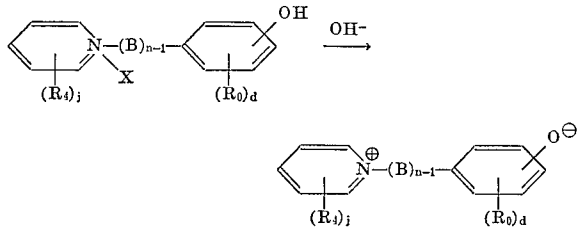
VIII.



wherein *n*, *j*, B, R_4, and R_0 are as previously defined, in an inert organic solvent (e.g., benzene, toluene, etc.), in approximately equimolar proportions. Advantageously, the reaction is heated up to reflux temperature for a period of several minutes or more, at which time the solid product precipitates from solution. The product is collected on a filter funnel and can be used, if desired, without further purification. However, for greater purity, the precipitate can be washed with a nonsolvent such as benzene and dried. The above-described process is illustrated more specifically in Examples 1–3 hereinafter.

As previously mentioned, the above-defined mordants of the invention function as "alkali-release" mordants in photographic layers. Thus, under appropriate conditions of pH (i.e., alkaline conditions), they form a zwitterion with resultant internal charge compensation and at the same time lose their ability to act as mordants, with release and subsequent removal of the mordanted dye from the system. 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, after processing, as do other compounds of similar mordanting ability, providing a neutral or mildly alkaline hypo bath is used.

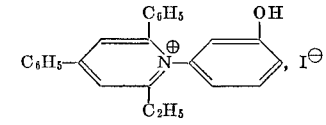
The formation of the zwitterion upon treatment in alkali is illustrated below with the structure of above Formula IV.



wherein *d*, *n*, *j*, B, R_4, R_0 and X are as previously defined.

The invention is further illustrated by the following examples describing the preparation and use of the mordanting compounds of the invention in photographic layers and elements.

Example 1.—1-m-hydroxyphenyl-2,4,6-triphenylpyridinium iodide



A one to one molar mixture of m-aminophenol and 2,4,6-triphenylpyrylium iodide in benzene was heated under reflux for two minutes at which time the solid product precipitated from soltuion. The product was then collected on a filter funnel and used without further purification. 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 - 2 - pyrazolin-5-one-(4)]pentamethineoxonol in gelatin, with no bleeding upon washing in water. The mordanted dye was bleached upon treatment of the coated gelatin layer (on a cellulose acetate film support) with a developer having the composition:

p-Methylaminophenol sulfate	g..	4.5
Sodium sulfite, desiccated	g..	90.0
Hydroquinone	g..	8.0
Sodium carbonate, monohydrated	g..	52.5
Potassium bromide	g..	5.0

Water to make 1 liter.

The bleaching was increased when the alkalinity of the developer was increased by the addition of sodium hydroxide. The residual yellow color was discharged by subsequent acidification of the gelatin layer. This was then treated with a fixing bath of the following composition:

Sodium thiosulfate	g..	240.0
Sodium sulfite, desiccated	g..	15.0
Acetic acid 28%	cc..	48.0
Boric acid, crystals	g..	7.5
Potassium alum	g..	15.0

Water to make 1 liter.

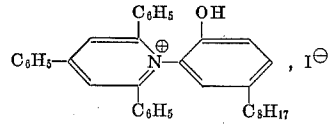
Result.—Mordanted well. Bleached effectively in the developer. Retained no hypo from the fixing bath.

The above results for Example 1 were made for hand coatings on cellulose acetate film support, the melts for which were prepared as follows:

To 10 cc. of 10% photographic gelatin melted at 40° C. was added 30 or 50 mgs. of mordant dissolved in 10 cc. of the appropriate solvent. The pH of the solution was adjusted to 4.5–5.0 with glacial acetic acid. To this was then added 10 mgs. of bis[3-methyl-1-p-sulfophenyl-5-pyrazolone-(4)]pentamethineoxonal, dissolved in the appropriate solvent with vigorous stirring. The pH of the melt was then readjusted to 6.0±0.1 with 2.5 N NaOH, a coating aid added, the total volume adjusted to 32 cc. with distilled water and the melt coated and dried.

The bleed test consisted of immersing a portion of the hand coating in stagnant, distilled water at 75° F. for two minutes and inspecting for signs of dye bleeding out of the gel layer. If no bleeding was detected, the immersion was repeated for another two minute interval. Bleachability was determined by immersion a portion of the hand coating in the developer for two minutes and observing the loss in color. Bleachability in the fixing bath was also determined, but none of the above samples bleached under these conditions. Thiosulfate retention values were determined by the Ross-Crabtree Method on unexposed film coatings, processed in a commercial Recordak film processing machine.

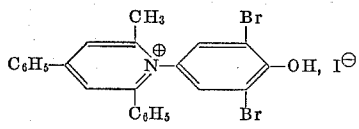
Example 2.—1-[2-hydroxy-5-(2,4,4-trimethyl-2-pentyl) phenyl]-2,4,6-triphenylpyridinium iodide



The procedure for preparing the above compound was the same as Example 1 above, except that 2-amino-4-(2,4,4-trimethyl-2-pentyl)phenol was substituted for the m-aminophenol.

This compound was tested as a mordant in similar manner with the same dye as in Example 1 above. The results indicated that this compound is an effective "alkali-release" mordant and does not retain any dye or measurable thiosulfate ion residue, after complete processing.

Example 3.—1-(3,5-dibromo-4-hydroxyphenyl)-4,6-diphenyl-2-picolinium iodide



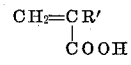
The above compound was prepared in accordance with the procedure of Example 1 above, except that the reactants were 2-methyl-4,6-diphenylpyrylium iodide and 4-amino-2,6-dibromophenol.

It was tested for mordanting ability, "alkali-release" properties and hypo retention in the same manner as that described in Example 1. The results showed good mordanting of the specified dye of Example 1, effective release and bleaching of the dye on development, and no measurable hypo retention from the fixing bath.

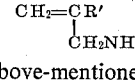
In place of the pyrylium compounds and the aminophenol compounds used in above Examples 1 to 3, there can be substituted an equivalent amount of any other of the intermediate compounds coming under Formulas IV and V above to give the corresponding compounds which likewise function effectively as "alkali-release" mordants in photographic layers. For example, other suitable pyrylium salt intermediates include 2-methyl-4,6-di-m (and p) tolylpyrylium halides, 2,6-dimethyl-4-(3-pyridyl) pyrylium halides, 2,4-diphenyl-6-propylpyrylium halides, 2-ethyl-4,6-di-p-tolylpyrylium halides, 2,4,6-triphenylpyrylium chloride, and the like, which are reacted with an aminophenol such as m-aminophenol, 2-amino-4-(2,4,4-trimethyl-2-pentyl)phenol, 4-amino-2,6-dibromophenol, etc., in accordance with the processes of the above examples.

The photographic elements prepared with the above-described 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. Patent 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:

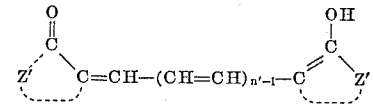


wherein R' represents an atom of hydrogen or a methyl group, and a salt of a compound having the general formula:

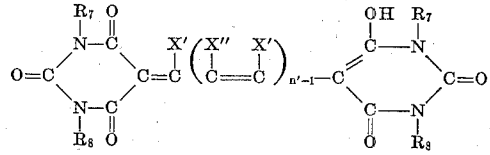


wherein R' has the above-mentioned meaning, such as an alkylamine salt. These monomers can further be polymerized with a third unsaturated monomer in an amount up to about 20 percent, and preferably from 5–15 percent of the total weight of monomer used, such as an ethylene monomer that is copolymerizable 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, Canadian Patent 690,133 issued July 7, 1964, having the formula:

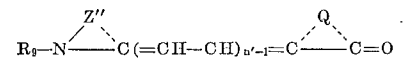


and more particularly the dyes of the formula:



wherein Z' 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_7 represents a carboxyalkyl group in which the carboxy substituent is attached to an alkyl group having from 1 to 2 carbon atoms, R_8 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 benzoxazolepyrazolone merocyanine dyes described in French Patent 1,359,682, issued Mar. 24, 1964, having the formula:



wherein R_9 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 sulfo-substituent on the benzene ring as well as one or more of the above-mentioned simple substituents, such that when R_9 represents an alkyl group, Z'' represents the sulfo-substituted benzoxazole nucleus and when R_9 represents a carboxyalkyl group or a sulfo-alkyl 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 sulfo-phenyl 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. Patent 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 - pyrazoline - 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 French Patent 1,359,924, issued Mar. 23, 1964, 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. Patent 2,739,888, issued Mar. 27, 1956, such as 3 - phenyl - 2 - phenylimino - 5 - o - sulfobenzal - 4-thiazolidone sodium salt, 5 - (4 - methoxy - 3 - sulfobanzal) - 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. Patent 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 - tetra - carboxylic 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. Patents 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. Patent 2,725,305, issued Nov. 29, 1955; a bisester of methanesulfonic acid such as 1,2-di(methanesulfonoxy)ethane as described in Allen and Laakso U.S. Patent 2,726,162, issued Dec. 6, 1955; 1,3-dihydroxymethylbenzimidazol-2-one as described in July, Knott and Pollak, U.S. Patent 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 Patent 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. Patent 2,950,197, issued Aug. 23, 1960; or 2,3-dihydroxydioxane as described in Jeffreys U.S. Patent 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.

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 mordant of Example 1 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 mordant of Example 1 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-sensitive layer **18** comprising gelatin, an acid substituted dye, and the mordant of Example 1 coated over layer **19**, and a blue-sensitive silver halide emulsion layer **17** coated over layer **18**.

Additional typical mordants of Formulas I and II used to advantage according to our invention are as follows:

Example:	Mordant
4	1 - dodecyl - 2,6 - diphenyl - 4 - (4 - hydroxyphenyl)pyridinium iodide.
5	3 - dodecyl - 6 - hydroxy - 2 - styrylbenzothiazolium iodide.
6	3 - benzyl - 1 - ethyl - 2 - [4 - (4' - hydroxy - α - naphthyl)butadienyl - 1, 4]benzimidazolium iodide.
7	3 - ethyl - 2 - [6 - (4 - hydroxyphenyl)-

Example: Mordant

hexatrienyl - 1,3,5] - β,β - naphthoxazolium iodide.

8 ——— N-octadecyl - N - (4 - hydroxy-α-naphthyl)pyrrolidinium iodide.

9 ——— N,N,N - tridodecyl - N - (2 - hydroxyphenyl)ammonium chloride.

10 ——— N,N - diphenyl - N - (2 - hydroxyphenyl) - N - decylammonium iodide.

11 ——— N - benzyl - N,N - didodecyl - N - (4-hydroxyphenyl)ammonium iodide.

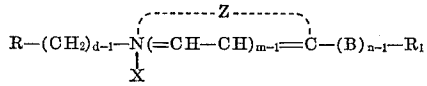
The mordants 4 through 11 are substituted for 1-m-hydroxyphenyl-2,4,6-triphenypyridinium iodide in Example 1 and are found to be excellent mordants which completely release acid dyes mordanted with them upon treatment with alkaline processing solutions. Mordants 4 through 8 are produced by the methods described previously herein. Mordants 9 through 11 are produced by alkylating the amine by methods well known in the art.

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.

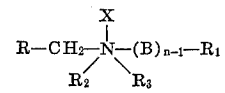
The invention has been described in detail with particular reference to preferred embodiments thereof but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic element comprising a support material having thereon a hydrophilic colloid layer containing at least one compound selected from those represented by the formula:

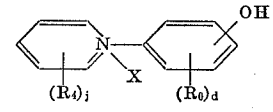


and



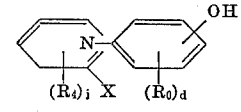
wherein *m* and *n* each represent an integer of from 1 to 2, R represents a member selected from the class consisting of the hydrogen atom, an alkyl group, and an aryl group, R_1 represents a member selected from the class consisting of an alkyl group, and an aryl group, R_2 and R_3 each represents a member selected from the class consisting of an alkyl group, and an aryl group, R_2 and R_3 together represent a divalent alkylene group of from 4 to 5 carbon atoms in the chain, X represents an acid anion, B represents a member selected from the class consisting of the group CH=CH, the group $(CH=CH)_2$, the group $(CH=CH)_3$, and the p-phenylene group, and Z represents the nonmetallic atoms necessary to complete a 5 to 6 membered heterocyclic nucleus selected from the class consisting of a thiazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a thionaphtheno-7',6',4,5-thiazole nucleus, an oxazole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a selenazole nucleus, a benzoselenazole nucleus, a naphthoselenazole nucleus, a thiazoline nucleus, a quinoline nucleus, an isoquinoline nucleus, a 3,3-dialkylindolenine nucleus, a pyridine nucleus, an imidazole nucleus, a benzimidazole nucleus, a naphthimidazole nucleus, a thiadiazole nucleus, an oxadiazole nucleus, a triazole nucleus and a tetrazole nucleus, provided that at least one of said R, said R_1 and Z contains a phenolic group, and wherein said compound has a molecular weight of at least 300, said element containing light-sensitive silver halide.

2. A light-sensitive photographic element comprising a support material having thereon a hydrophilic colloid layer containing at least one substantially non-diffusible salt of a water-soluble acid dye with a mordant compound of the formula:



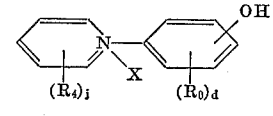
wherein *j* represents an integer of from 1 to 3, *d* represents an integer of from 1 to 2, R_4 and R_0 each represents a member selected from the class consisting of the hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a 2-thienyl group, a 2-pyrryl group, a 2-indolyl group, a 3-indolyl group, a 2-furyl group, a 3-pyridyl group, and a 4-pyridyl group, and X represents an acid anion, said compound having a molecular weight of at least 300, said element containing light-sensitive silver halide.

3. A light-sensitive photographic element comprising a support material having thereon at least two hydrophilic colloid layers, at least one of said hydrophilic colloid layers being a light-sensitive silver halide emulsion layer and at least one of said hydrophilic layers containing at least one nondiffusible salt of a water-soluble acid dye with a compound of the formula:



wherein *j* represents an integer of from 1 to 3, *d* represents an integer of from 1 to 2, R_4 and R_0 each represents a member selected from the class consisting of the hydrogen atom, a halogen atom, an alkyl group, aryl group, an alkoxy group, an aryloxy group, a 2-thienyl group, a 2-pyrryl group, a 2-indolyl group, a 3-indolyl group, a 2-furyl group, a 3-pyridyl group, and a 4-pyridyl group, and X represents an acid anion, said compound having a molecular weight of at least 300.

4. A light-sensitive photographic element comprising a support material having coated thereon at least one light-sensitive silver halide emulsion layer and having coated over said emulsion layer a hydrophilic colloid layer containing at least one substantially non-diffusible salt of a water-soluble acid dye with a compound of the formula:



wherein *j* represents an integer of from 1 to 3, *d* represents an integer of from 1 to 2, R_4 and R_0 each represents a member selected from the class consisting of the hydrogen atom, a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group, a 2-thienyl group, a 2-pyrryl group, a 2-indolyl group, a 3-indolyl group, a 2-furyl group, a 3-pyridyl group, and a 4-pyridyl group, and X represents an acid anion, said compound having a molecular weight of at least 300.

5. A photographic element of claim 2 wherein said hydrophilic colloid layer comprises gelatin.

6. A photographic element of claim 2 wherein said compound is 1-(3,5-dibromo-4-hydroxyphenyl) - 4,6 - dium iodide.

7. A photographic element of claim 2 wherein said compound is 1-[2-hydroxy-5-(2,4,4-trimethyl-2-pentyl) phenyl]-2,4,6-triphenylpyridinium iodide.

8. A photographic element of claim 2 wherein said

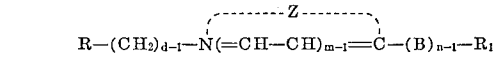
compound is 1-(3,5-dibromo-4-hydroxyphenyl) - 4,6 - diphenylpicolinium iodide.

9. A photographic element of claim **2** wherein said acid dye is bis[3-methyl-p-sulfophenyl-2-pyrazolin-5-one-(4)]-pentamethineoxonol and said compound is 1-m-hydroxyphenyl-2,4,6-triphenylpyridinium iodide.

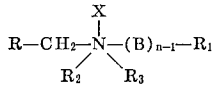
10. A light-sensitive photographic element according to claim **2** wherein at least one of said dye components of said salts is a dye selected from the group consisting of 4 - [(3 - ethyl - 2(3H) - benzoxazolylidene)ethylidene]-3-methyl - 1 - p-sulfophenyl - 2 - pyrazolin-5-one monosulfonated, bis(1-butyl-3-carboxymethyl-5-barbituric acid)trimethineoxonol, 4-[4-(3-ethyl-2(3H)-benzoxazolylidene)-2 - butenylidene]-3-methyl-1-p-sulfophenyl-2-pyrazolin-5-one monosulfonated, 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 and bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)]pentamethineoxonol.

11. A light-sensitive photographic element according to claim **2** wherein at least one of said dye components of said salts is a dye selected from the group consisting of 4-[(3 - ethyl - 2(3H) - benzoxazolylidene)ethylidene] - 3 - methyl - 1 - p - sulfophenyl-2-pyrazolin-5-one monosulfonated, bis(1-butyl-3-carboxymethyl-5-barbituric acid) trimethineoxonol, 4-[4-(3-ethyl-2(3H)-benzoxazolylidene)-2-butenylidene]-3-methyl - 1 - p-sulfophenyl-2-pyrazolin-5 - one monsoulfonated, 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 and bis[3-methyl-1-(p-sulfophenyl)-2-pyrazolin-5-one-(4)]pentamethineoxonol, and wherein the said hydrophilic colloid layer comprises gelatin.

12. An element comprising a support material having thereon a hydrophilic colloid layer containing a salt of a water-soluble acid dye and at least one compound selected from those represented by the formula:



and



wherein *m* and *n* each represent an integer of from 1 to 2, R represents a member selected from the class consisting of the hydrogen atom, an alkyl group, and an aryl group, R_1 represents a member selected from the class consisting of an alkyl group, and an aryl group, R_2 and R_3 each represents a member selected from the class consisting of an alkyl group, and an aryl group, R_2 and R_3 together represent a divalent alkylene group of from 4 to 5 carbon atoms in the chain, X represents an acid anion, B represents a member selected from the class consisting of the group CH=CH, the group $(CH=CH)_2$, the group $(CH=CH)_3$, and the p-phenylene group, and Z represents the nonmetallic atoms necessary to complete a heterocyclic nucleus having from 5- to 6-members in the heterocyclic ring, provided that at least one of the said R, said R_1, and said Z groups contains a phenolic group, and wherein said compound has a molecular weight of at least 300.

References Cited

UNITED STATES PATENTS

3,016,306	1/1962	Mader et al.	96—84 XR
3,271,148	9/1966	Whitmore	96—84 XR

NORMAN G. TORCHIN, *Primary Examiner.*

R. SMITH, *Assistant Examiner.*

U.S. Cl. X.R.

96—057, 029; 117—167

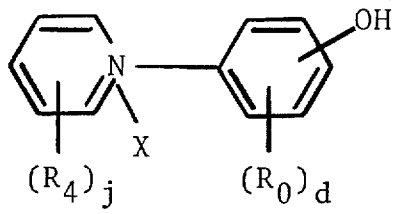
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,425,833 February 4, 1969

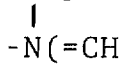
Robert C. Taber et al.

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

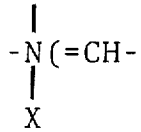
Column 14, lines 32 to 37, the formula should appear as shown below:



same column 14, lines 70 and 71, "1-(3,5-dibromo-4-hydroxyphenyl-4,6-di-ium iodide" should read -- 1-m-hydroxyphenyl-2,4,6-triphenylpyridinium iodide --. Column 16, lines 3 to 6, that part of the formula reading



should read



Signed and sealed this 5th day of May 1970.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents