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PROCESSES OF COLOR PHOTOGRAPHY

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This invention relates to photography and more particularly to photographic color processes and compositions and elements useful therein. Still more particularly it relates to photographic color processes, compositions and elements wherein polyvinyl acetals are used as dye intermediates or color formers. Still more particularly it relates to water permeable colloid layers comprising as an essential dye component a polyvinyl acetal capable of reacting with a diazo compound to form a dye. The invention further relates to developer and treating solutions containing such acetals and to their preparation and use, particularly in photographic development processes.

This invention has for an object the provision of new and useful photographic compositions containing dye intermediates or color formers which are immobile in water permeable colloid layers, such as gelatin layers. A further object is to provide photographic compositions and elements which contain novel polymeric dye intermediates. A still further object is to provide a new photographic color process, especially a photographic color development process involving the use of polyvinyl acetals. Another object is the preparation of photographic emulsions which contain new and improved water-soluble dye intermediates or color formers which yield dyes by coupling with the oxidation products of photographic developing agents or by treatment with aromatic or heterocyclic diazo compounds. Other objects are to provide alternative photographic compositions and processes and to contribute a general advance in the art. Still other objects will be apparent from the following description of the invention.

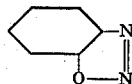
The above objects are accomplished by the preparation and use of photographic compositions and elements containing polyvinyl acetals which are capable of reacting with a diazo compound to form a dye.

In a more limited sense, they are accomplished by the preparation and use in photographic colloid layers and photographic developing and treating solutions of polyvinyl acetals formed from aldehydes which are capable of reacting with a diazo compound to form a dye. The aldehyde or ketone nuclei may thus have an aromatic nucleus such as a benzene ring containing a phenolic hydroxyl group or an amino group either substituted or unsubstituted, e. g. an alkylamino, dialkylamino, arylamino, or alkylaryl amino group, and which are further characterized in that they have a reactive position ortho or para to the mentioned groups, or have an active meth-

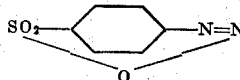
ylene group. The ortho or para positions may be reactive by being unsubstituted or by having a replaceable group such as a halogen atom, e. g. chlorine or a sulfonic acid group. One or more of such groups may be present.

In one important aspect of the invention, it involves the preparation and use of photographic compositions, e. g. colloid layers, light sensitive emulsion layers and coating compositions therefor, and developer solutions containing polyvinyl acetals which are soluble in dilute alkaline solutions and are capable of coupling with diazo compounds to form a dye.

The acetals of this invention, because of their structure and the nature of the aldehyde nuclei, couple with diazo compounds to form a dye. As examples of such latter compounds, mention is made of the diazonium salts, syndiazotates, diazo-anhydrides and diazo inner salts of the general formula $A-N=N-X$, wherein A is an aromatic or an unsaturated heterocyclic residue or compounds resulting from intramolecular elimination of HX therefrom. X may suitably be OH, or salts thereof, such as ONa, OK and ONH₄, or salt forming anions, such as Cl⁻, Br⁻, NO₃⁻, and SO₃H⁻. Elimination of HX is exemplified by diazotized o-aminophenol of the formula



and by diazotized sulfanilic acid of the formula



The acetals furthermore react with the oxidation products of an aromatic amino developing agent under conditions of the usual photographic development processes to form a dye. The acetals which contain as solubilizing groups carboxylic or sulfonic acid groups constitute the preferred embodiment of the invention. These groups need not be present in the nuclei containing color forming groups which are joined through acetal linkages to the polyvinyl alcohol nuclei, but may be in radicals free from color forming groups joined to the latter nuclei through acetal linkages.

The dye-forming polyvinyl acetals of this invention are conveniently prepared by the following general manner. One method comprises reacting polyvinyl alcohol under conditions suitable for the formation of an acetal, with an aldehyde capable of reacting with a diazo compound

to produce a dye. The most important of such aldehydes are those containing an aromatic nucleus on which is substituted a phenolic hydroxyl, amino, including unsubstituted and substituted amino groups, e. g. alkylamino, arylamino, or mixed alkylaryl amino group, at least one of the positions oriented by such groups (ortho and para) being reactive. Thus, the positions may be unsubstituted or have a replaceable group, e. g. chlorine, sulfonic acid, etc. Other suitable aldehydes are those having active methylene groups, such as, for example, those containing pyrazolone and acetoacetamino groups.

The polyvinyl acetals just described are also capable of reacting with the oxidation products of photographic aromatic primary amino developing agents to form azomethine or quinoneimine dyes including indophenol, indoaniline, and indamine dyes.

An alternative method comprises reacting an aldehyde which does not have the above-described structure with a polyvinyl alcohol and then chemically modifying the acetal so that it has the desired structure. The methods are illustrated below.

These polymeric dye intermediates may be incorporated in a colloid binding agent including a light-sensitive emulsion and coated on a support by any of the general or known methods to form an element having a light sensitive or photographic layer. After exposure, the intermediates are converted into dyes, for example, by development of the images produced with a color-forming developer, such as p-aminodiethylaniline, or by some other suitable procedure such as a treatment with aromatic diazo compounds.

The polyvinyl acetals capable of reacting with diazo compounds may be incorporated in various types of colloid binding agents which are capable of forming water permeable films or layers such as gelatin, agar agar, or polyvinyl alcohol by forming aqueous or alcoholic dispersions or emulsions of the same and coating them upon a support which may be a transparent or non-transparent support or film base. Suitable supports include cellulose derivatives, e. g. cellulose acetate, cellulose nitrate, cellulose-aceto-propionate, etc., synthetic resins, e. g. polyvinyl acetals such as polyvinylisobutyraldehyde acetal; polymeric compounds such as nylon and paper, etc. The layers may be deposited on a subbing layer which is used to anchor silver halide emulsion layers on a film base or on another colloid layer which may be a gelatin silver halide layer. One or more of such layers containing one or more of the novel polyvinyl acetals hereof may be present in the resulting element.

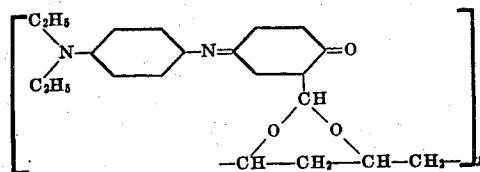
The polyvinyl acetals hereof may be incorporated into colloid compositions containing light sensitive materials, e. g. silver halides and photographic layers formed on suitable supports as described in the preceding paragraph. A plurality of such layers may form a multilayer photographic element. The polyvinyl acetals of the respective layers should, however, be capable of forming different colored azo and/or azomethine or quinoneimine dyes.

The invention will be further illustrated but is not intended to be limited by the following examples in which the parts stated are parts by weight.

Example I

Thirty-two parts of polyvinyl alcohol, 45 parts of salicylaldehyde, 525 parts of glacial acetic acid,

and 5 parts of 85% phosphoric acid were stirred and heated at 60-70° C. for nine hours. The reaction product obtained in translucent solution was precipitated by addition of ethanol and water and was washed successively with water and methanol and was dried. The yield of dry product amounted to 39 parts. This resin, when placed in a photographic emulsion, e. g. a gelatin silver-iodo-bromide emulsion, exposed and developed with p-aminodiethylaniline, gave a blue-green image. This color is presumably due to coupling with an oxidation product of the developer at the free position para to the phenolic hydroxyl, giving an indophenol dye of the probable structure (assuming polyvinyl alcohol to be a 1,3-glycol):



Example II

The same ingredients as in Example I were used. However, after stirring and heating for four hours at 60-70° C., 4.5 parts of isobutyraldehyde was added. On heating one hour further, the translucent, hazy solution at first obtained became clear. The resin was worked up in the manner described under Example I and was found to have the same properties in regard to dye formation, but was of lower softening point and enhanced solubility.

Example III

Twenty-two parts of polyvinyl alcohol, 23 parts of redistilled salicylaldehyde, 250 parts of glacial acetic acid, and 2 parts of 85% phosphoric acid were heated and stirred at 65° C. for four and one-half hours, at which time a milky solution had formed. Nine and four-tenths parts of phthalaldehydic acid was then added and heating was continued for three hours further. The resin was precipitated by addition of ethanol and water and was washed successively with water and methanol and was dried. The yield of dry product amounted to 26 parts. This resin is soluble in aqueous alkali and may thus be suitably introduced into photographic emulsions. When a silver halide emulsion, e. g. a silver-iodo-bromide emulsion containing this product is coated on a suitable support, is exposed and developed with p-methylaminophenol, a black and white negative is obtained. Subsequent development, after re-exposure, with p-aminodiethylaniline gives a blue-green positive after removal of silver and silver salts. The dye thus obtained, in common with those from the resins of Examples 1 and 2, transmits little or no red light and is thus eminently suitable for use in subtractive processes of color photography. In spite of its solubility in dilute alkali, the dye is not at all removed by the alkaline processing baths and may even be leached for long periods in 5% sodium carbonate solution without removal.

Example IV

Twenty-two parts of polyvinyl alcohol, 250 parts of glacial acetic acid, 23 parts of salicylaldehyde, 9.4 parts of phthalaldehydic acid, and 4 parts of 85% phosphoric acid were heated and stirred on a water bath maintained at 65° C. for five and one-quarter hours. A clear, light yellow

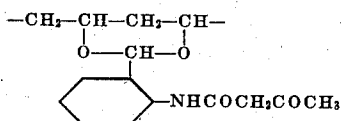
low solution was obtained from which the resin was precipitated by the addition of methanol. After washing several times with methanol and cold water, the product was dried in a vacuum oven. Twenty-four parts of white, finely divided resin were obtained. The product was dissolved in dilute alkali and coated in a photographic silver halide emulsion sensitive only to blue light. After exposure and development with p-methyl-amino-phenol and fixation, a yellow dye was produced throughout the whole film by treatment with diazotized p-nitraniline. The film may then be differentially bleached by any selective bleaching process, e. g. according to the process of Christensen (c. f. Br. Patent 133,034 or U. S. Patent 1,517,049). After removal of the silver image there will remain a yellow positive image.

Example V

Forty-four parts of polyvinyl alcohol, 46 parts of m-hydroxy-benzaldehyde, 500 parts of glacial acetic acid, 18.4 parts of phthalaldehydic acid, and 8 parts of 85% phosphoric acid were stirred and heated at 65° C. for eleven hours. At this time 1.6 additional parts of 85% phosphoric acid was added and heating continued for ten hours further. Most of the resin at this stage was in the form of a gelatinous mass. This was dissolved in dioxane and reprecipitated in fibrous form with water. After washing the product with water and aqueous methanol and drying, 58 parts of resin were obtained. Treatment with oxidized p-aminodiethylaniline gave a blue-green dye.

Example VI

Eight parts of polyvinyl alcohol, 84 parts of glacial acetic acid, 8 parts of o-nitrobenzaldehyde, 6 parts of phthalaldehydic acid, and 3.2 parts of 85% phosphoric acid were heated and stirred at 65° C. for five hours. The resin was precipitated by addition of methanol and cold water and was washed. It was then dissolved in dilute sodium hydroxide solution and the nitro group of the acetal formed was reduced with sodium hydrosulfite to the amino group. After neutralizing, the resin was precipitated with acetone, was washed, dried, and dissolved in formamide. Twelve parts ethyl aceto-acetate and 1.9 parts pyridine were added and the solution was heated for five hours on a steam bath to form the acetoacetanilide of the acetal having the probable unit structure:



After reprecipitating with acetone, washing, and drying, the product was introduced into a photographic silver halide emulsion which was subsequently coated on a cellulose acetate film, exposed and developed with p-aminodimethylaniline, a yellow dye being formed.

Example VII

Twenty-two parts of polyvinyl alcohol was suspended in 250 parts of glacial acetic acid. To this were added 15.5 parts of 2-hydroxy-3-methylbenzaldehyde, 19 parts of phthalaldehydic acid, and 4.3 parts of 85% phosphoric acid and the mixture was heated on a water bath at 65° C. with vigorous stirring for 11 hours. At the end of this time a thick translucent solution had formed. The resin was precipitated from the solution with methanol and was washed in meth-

anol and in water. Upon incorporation of the acetal in an emulsion after the manner set forth in Example VI, and after subsequent exposure and development with p-aminodiethylaniline, a blue-green color was formed.

Example VIII

In place of the 2-hydroxy-3-methylbenzaldehyde of the preceding example, 12 parts of 3-chlor-2-hydroxybenzaldehyde was used. After 5 hours heating at 65° C. the resin was precipitated from the reaction mixture and washed with methanol and water. Upon incorporation of the acetal in an emulsion and after treatment of the emulsion as set forth in Example VI, a blue-green color was formed.

Example IX

The procedure of Example VII was carried out, using the following quantities of reactants:

	Parts
Polyvinyl alcohol	22
5-chlor-2-hydroxybenzaldehyde	20
Phthalaldehydic acid	19
Glacial acetic acid	250
85% phosphoric acid	6.8

Five and a half hours heating at 65° C. on a water bath was required to complete the reaction. The reaction product was precipitated with methanol, washed with methanol, then with water. This yielded a white solid soluble in dilute alkaline solutions. The acetal was incorporated in a silver halide emulsion which was treated after the manner set forth in Example VI, whereupon a blue-green color was formed.

Example X

Twenty-five parts of 3-allyl-2-hydroxybenzaldehyde, 19 parts of phthalaldehydic acid, 22 parts of polyvinyl alcohol, 250 parts of glacial acetic acid and 8.5 parts of 85% phosphoric acid were stirred and heated on a water bath at a temperature of 65-70° C. for 7.5 hours. At the end of this time a clear, homogeneous solution was obtained. The resin was precipitated by addition of methanol, was redissolved in dioxan, and was finally precipitated in fibrous form by pouring into water. The product was thoroughly washed in water and dried. The polyvinyl acetal was soluble in aqueous alkali and, when incorporated in a photographic silver halide emulsion, a blue-green image was formed after exposure and development with p-aminodiethylaniline.

Example XI

Six parts of 1-hydroxy-2-naphthaldehyde, 4 parts of phthalaldehydic acid, 6.5 parts of polyvinyl alcohol, 63 parts of glacial acetic acid and 3.4 parts of 85% phosphoric acid were heated and stirred on a water bath at a temperature of 65-70° C. for 10 hours. The resin was then precipitated by stirring in methanol and was washed thoroughly with methanol and finally with water. The polyvinyl acetal was found to be soluble in dilute alkali and, when incorporated in a photographic silver halide emulsion which was exposed and developed with p-aminodiethylaniline, a blue-green picture was obtained.

Example XII

A mixture of 33 parts of 3,5-dichlorosalicylaldehyde, 22 parts of polyvinyl alcohol, 263 parts of glacial acetic acid and 5 parts of 85% phosphoric acid was stirred and heated on a water

Example XIII

Example XIV

Example XV

Example XVI

Example XVII

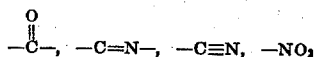
Example XVIII

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Other polymeric color formers which have been found as a result of this invention to be of value in color photographic processes are the polyvinyl acetals of 1,4-hydroxy-naphthaldehyde, 3-di-

methylaminobenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde, 1-(3-formylphenyl)-3-methyl-5-pyrazolone, 1-(4-formylphenyl)-3-methyl-5-pyrazolone and 1-(2-formylphenyl)-3-methyl-5-pyrazolone, o-, m-, and p-acetoacetaminobenzaldehyde, 3-brom-2-hydroxybenzaldehyde, 2-hydroxy-3-nitrobenzaldehyde, 6-hydroxy-2-methylbenzaldehyde, and 2-hydroxy-5-methylbenzaldehyde. The acetals may be suitably prepared from aldehydes in which the aldehyde group is not directly substituted on the aromatic nucleus, for example, as in the polyvinyl acetal of p-hydroxyphenylacetaldehyde.

Acetals containing active methylene groups for color coupling have been described above and in the working examples. An active methylene group is a methylene group having one hydrogen replaceable in azo coupling reactions or replaceable by alkali metal in alkaline solution. This group derives its reactivity by reason of the fact that it is attached by a single valence directly to one of the following groups:



the remaining valence of the active methylene groups being also attached to one of these same unsaturated groups either (1) directly or (2) through an even-numbered chain of multibonded carbon atoms, each carbon of which is part of a conjugated system of which the atoms connected by the multiple bond in the above unsaturated groups are an integral part.

It has been found that an especially advantageous modification of the invention is obtained when acidic salt forming groups are introduced into the polymeric color former. Particularly suitable groups are carboxyl and sulfonic acid groups, the introduction of which leads to products soluble in dilute sodium carbonate solutions. The introduction of phenolic hydroxyl and mercaptan groups in sufficient number also promotes alkali solubility but the resins are not in general soluble in solutions made alkaline with carbonates. Since these products may conveniently be introduced into photographic emulsions from dilute carbonate solutions, they are uniquely suitable for incorporation into the slightly alkaline photographic emulsions where they manifest full compatibility and thus lead to bright, intense colors free from haze. Since acetal formation need not proceed to substantial completion to produce a satisfactory color forming product, the acidic salt forming groups may conveniently be introduced by reaction of the unreacted portion of the polyvinyl alcohol molecule. Procedures of this type are illustrated in the examples.

The products are most conveniently solubilized by reaction of the polyvinyl alcohol or partial acetal thereof with aldehydes containing carboxyl or sulfonic acid groups. Suitable compounds for this purpose are phthalaldehydic acid, benzaldehyde-o-sulfonic acid, glyoxylic acid and propionaldehyde beta-sulfonic acid. In place of acetal formation with aldehydo-acids, the acidic salt-forming groups may also be introduced by any other suitable reaction such as half-esterification with anhydrides or dibasic acids, e. g. phthalic or maleic anhydrides, or etherification with halogenated acids, e. g., chloroacetic acid. In general, the introduction of the color forming nuclei and the acidic salt forming groups into the polyvinyl alcohol molecule may proceed simultaneously or successively in any desired order. The acidic salt forming group may form an integral part of the

color forming nucleus as in the case of 3-carboxy-2-hydroxy-benzaldehyde, in which case the reaction of one compound with polyvinyl alcohol introduces both the color forming nucleus and the acidic salt forming group. In certain cases the acidic salt forming group may be introduced by sulfonation of the polymer.

It is often found that acetalization of polyvinyl alcohol with the complex aromatic aldehydes contemplated in the present invention occurs to only a limited extent. In general, only a small percentage of acetal formation is necessary to obtain a compound with color-forming properties, but the physical properties of the polymer, e. g. solubility, may not be all that is desired. In this case, additional reaction with the partially acetalized product may be carried out to give the polymer the desired properties. This additional reaction is preferably further acetal formation with a different aldehyde or cyclic ketone or a mixture of aldehydes and/or cyclic ketones, as illustrated in the examples, but may be any other suitable reaction, such as half-esterification with dibasic acids or etherification with halogenated acids. Furthermore, the acetal formation may be carried out upon polyvinyl alcohol or upon a partially hydrolyzed polyvinyl ester, and the hydrolysis products of interpolymers of vinyl esters and other unsaturated compounds. The acetals may also be prepared from polyvinyl esters, e. g. polyvinyl acetate, by simultaneous hydrolysis and acetalization. They may also be prepared from a mixture of aldehydes by simultaneous or stepwise reaction. Acetal interchange may also be resorted to.

Among the suitable acetal forming compounds which may be used as modifying constituents for the acetals are formaldehydes, acetaldehyde, propionaldehyde, n- and iso-butyraldehyde, etc. Suitable cyclic ketones include cyclohexanone, 3-methylcyclohexanone, 3,5-dimethylcyclohexanone, 2-methylcyclohexanone, 1-ethylcyclohexanone, 2-bromocyclohexanone and oxotetrahydronaphthalenes. The aliphatic aldehydes are preferred.

The polyvinyl acetals of this invention have a degree of acetalization from the color-forming aldehyde used of about 10 to about 50% and preferably about 20 to about 30%. The degree of acetalization resulting from the non-color-forming aldehyde, that is, from the modifying or solubilizing aldehyde, is about 10 to about 50%, preferably 20 to 30%. The total degree of acetalization is 40 to 75% and usually 50 to 70%. By "degree of acetalization" is meant the percentage of original hydroxyl (or ester) groups which have been converted to acetal groups.

Practically any condensation catalyst of acid reaction may be employed. Suitable catalysts include mineral acids, e. g. phosphoric, hydrochloric, perchloric and sulfuric; organic acids, e. g. p-toluenesulfonic acid; acid reacting salts, e. g. aluminum chloride; and boron trifluoride. Phosphoric acid is preferred, being one of the best catalysts from the standpoint of the color of the resulting product.

While acetic acid is the preferred solvent for the preparation of acetals of this invention, other organic solvents may be resorted to. As further examples of suitable solvents, mention is made of methyl, ethyl, propyl, isopropyl, and n-butyl alcohols and dioxane.

The color yielding elements may contain light sensitive layers composed of simple or mixed silver halides which may contain the usual sensi-

tizers, desensitizers, stabilizers, fog inhibitors, emulsion hardeners, etc. Suitable types include silver chloride, silver bromide, silver chlorobromide, silver chloride-bromide-iodide, silver bromide-iodide, etc., which may contain cyanine, carbocyanine, polymethine cyanine, cyazine, carbocyzine, pseudocyanine, kryptocyanine, merocyanine, rhodanine, etc. salts and bases. The silver halide layers may be anchored to the supports by means of the usual subbing solutions which are also useful for anchoring dye component layers free from silver salts to bases.

The products of this invention are not limited in their utility to any one process of color photography. They may be used with color coupling developing agents in general and are not limited to those specifically described in the examples. Hydrazines such as those described in U. S. P. 2,220,929 and the color coupling developers of U. S. P. 2,163,820 can be used. The diamino aryl compounds such as paraphenylene-diamine and its substitution products constitute a practical class of such agents. These developers may be substituted in the amino groups as well as in the ring, preferably the former, to constitute compounds such as the mono- and di-alkyl arylenediamines, including the mono- and di-alkyl naphthylenediamines, alkyl phenylenediamines and alkyl toluylenediamines. The compounds, of course, must have one free primary or unsubstituted amino group which enables the oxidation product of the developer to couple with the color-forming compounds. As examples of developers of the class described, there may be mentioned p-aminodiethylaniline, 1,4-naphthylenediamine, 4-diethylamino-1-naphthylamine and their acid salts. The salts of the bases which may be organic or inorganic are, in general, more soluble and more stable than the free bases. The hydrochlorides and sulfates have great utility.

All of the acetals couple with diazo compounds so that they are, therefore, suitable for transformation to azo dyes, followed by differential bleaching in the presence of silver images, as known in the art. These compounds are also especially useful in the azo process of application, Serial No. 335,416, filed May 15, 1940, now U. S. Patent 2,297,732.

The above-described acetals may also be incorporated in colloid layers sensitized by treatment with bichromate. Any colloid capable of this sensitization may be used, as, for example, gelatin, gum arabic or albumen. Appropriate methods of developing dye images after exposure then include the process of removal of the unexposed colloid with hot water and dye development of the exposed portions with p-nitrosoaniline or its derivatives and the process of development with dye coupling developers.

All of the compounds contemplated in the invention possess the major advantage of being nonmigratory in emulsion layers. The significance of this fact is that incorrect color values cannot then arise from migration of one of the "color formers" into a layer adjacent to the one in which it is placed. Furthermore, no bleeding can take place into processing baths. This observation is striking when it is recalled that the preferred products are soluble in dilute alkali and certain of the processing solutions are alkaline in nature.

The polyvinyl acetals hereof have the further advantage that they do not have a deleterious effect on the photographic characteristics of sil-

ver halide emulsion layers of photographic elements.

This application is a continuation-in-part of application Serial No. 233,480, filed October 5, 1938, now U. S. Patent 2,310,943, which covers the polyvinyl acetals hereof as new compounds.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that we do not limit ourselves to the specific embodiments herein except as defined by the appended claims.

We claim:

1. A photographic element bearing a water-permeable colloid layer containing a light-sensitive material and a polyvinyl acetal capable of reacting with a diazo compound to form an azo dye.

2. A photographic element bearing an emulsion layer containing a light-sensitive material and a polyvinyl acetal capable of reacting with a diazo compound to form an azo dye.

3. A photographic element bearing an emulsion layer containing a light-sensitive silver halide material and a stratum comprising a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being capable of reacting with a diazo compound to form an azo dye.

4. A photographic element bearing an emulsion layer containing a light-sensitive material and a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being capable of reacting with the oxidation products of an aromatic primary amino developing agent to form a dye.

5. A photographic element bearing an emulsion layer containing a light-sensitive silver halide material and a stratum comprising a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being soluble in dilute alkaline solutions and is capable of reacting with a diazo compound to form an azo dye.

6. A photographic element bearing an emulsion layer containing a light-sensitive silver halide material and a stratum comprising a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being soluble in dilute alkaline solutions and is capable of reacting with a diazo compound to form an azo dye and with the oxidation products of an aromatic primary amino developing agent to form a dye taken from the group consisting of azomethine and quinoneimine dyes.

7. A photographic element of the type set forth in claim 5 wherein the light-sensitive material comprises silver chloride.

8. A process of producing dye images comprising exposing a photographic element containing a light-sensitive material and a polyvinyl acetal which is capable of reacting with a diazo compound to form an azo dye and treating the element with an aromatic primary amino developing agent.

9. A process of producing dye images comprising exposing a photographic element containing a light-sensitive silver halide material and a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being capable of reacting with an aromatic diazo compound to form an azo dye, treating the element with a diazo compound and then differentially bleaching the azo dye thus formed in the image areas.

10. A photographic element bearing a water permeable colloid layer containing a light-sensitive silver halide material and a polyvinyl acetal of polyvinyl alcohol with an aldehyde, said acetal being capable of reacting with a diazo compound

to form an azo dye, said acetal being of a carbonyl compound containing free acid radicals taken from the group consisting of carboxylic and sulfonic acid radicals.

11. A photographic element bearing a water permeable colloid layer containing a light-sensitive material and a polyvinyl acetal capable of reacting with a diazo compound to form an azo dye, said acetal containing acetal linkages from an aromatic aldehyde compound containing free acid radicals taken from the group consisting of carboxylic and sulfonic acid radicals.

12. A photographic element bearing a water permeable colloid layer containing a light-sensitive silver halide material and a polyvinyl acetal capable of reacting with a diazo compound to form an azo dye, said acetal containing acetal linkages from a carbonyl compound containing free acid radicals taken from the group consisting of carboxylic and sulfonic acid radicals, and acetal linkages from an aldehyde capable of coupling with a diazo compound to form an azo dye.

13. A photographic element bearing at least one water-permeable colloid layer having dispersed therethrough a polyvinyl acetal capable of reacting with a diazo compound to form an azo dye.

14. An element as set forth in claim 13, containing a stratum of a light sensitive material.

15. A process of producing dye images which comprises exposing a photographic element bearing a light sensitive silver halide emulsion layer containing a polyvinyl acetal of salicylaldehyde and benzaldehyde-ortho-sulfonic acid and devel-

oping the exposed element in a developer solution containing an aromatic primary amino color developing agent.

16. A photographic element bearing a water permeable colloid layer containing a reducible silver halide and a polyvinyl acetal of salicylaldehyde and benzaldehyde-ortho-sulfonic acid.

17. A process of producing dye images which comprises exposing a photographic element bearing a light sensitive silver halide emulsion layer containing a polyvinyl acetal of 1-hydroxy-2-naphthaldehyde and phthalaldehydic acid and developing the exposed element in a developer solution containing an aromatic primary amino color developing agent.

18. A photographic element bearing a water permeable colloid layer containing a reducible silver halide and a polyvinyl acetal of 1-hydroxy-2-naphthaldehyde and phthalaldehydic acid.

19. A process of producing dye images which comprises exposing a photographic element bearing a light sensitive silver halide emulsion layer containing a polyvinyl acetal of 3,5-dichlorosalicylaldehyde and benzaldehyde-ortho-sulfonic acid and developing the exposed element in a developer solution containing an aromatic primary amino color developing agent.

20. A photographic element bearing a water permeable colloid layer containing a reducible silver halide and a polyvinyl acetal of 3,5-dichlorosalicylaldehyde and benzaldehyde-ortho-sulfonic acid.

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