

## UNITED STATES PATENT OFFICE

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## POLYVINYL ACETALS

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This invention relates to new polymeric products and their use in color photography. More particularly it relates to acetals of polyvinyl alcohol and aldehydes which are capable of coupling with a diazo compound. Still more particularly it relates to color forming photographic emulsions containing said acetals and to photographic elements bearing such emulsions. The invention also relates to photographic development processes and to finished colored photographs.

This invention has for an object the production of new color formers which are useful in color photography. A further object is the preparation of photographic emulsions which contain new and improved water-insoluble dye-formers 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. A further object is the provision of new photographic developing processes. A still further object is the preparation of photographic elements bearing an emulsion which contains novel color formers which do not migrate. A still further object is the preparation of multilayer photographic films containing color-formers which do not migrate from layer to layer or into the processing baths. A still further object is the preparation of finished photographs which contain stable dyed images which are formed of water insoluble dyes. Other objects include the preparation of colored photographs and color forming emulsions upon opaque or transparent supports and a general advance in the art. Still other objects will appear hereinafter.

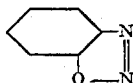
The above and other objects are accomplished by the following invention which involves the preparation and use in photographic processes and emulsions of polyvinyl acetals which are capable of coupling with a diazo compound to form a dye.

In a more limited sense, they are accomplished by the preparation and use in photographic processes and emulsions of polyvinyl acetals either having an aromatic nucleus containing a phenolic hydroxyl, alkoxy, aryloxy, amino, alkylamino, arylamino or mixed alkylaryl amino group and which are further characterized in that they have a reactive position ortho or para to mentioned groups, or having an active methylene group.

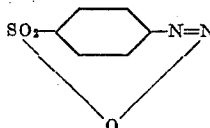
In a still more limited sense which represents a preferred embodiment of the invention, they are accomplished by the preparation and use of

polyvinyl acetals which are soluble in dilute alkaline solutions and are capable of coupling with diazo compounds to form a dye which is likewise soluble in dilute alkaline solutions.

The acetals of this invention because of their structure will couple with diazo compounds. As examples of such compounds, mention is made of the diazonium salts, syn-diazotates, 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  $ONH_4$ , or salt forming anions, such as  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ , and  $SO_4H^-$ . 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. They also react with nitroso compounds produced in situ or preformed by other processes. By "polyvinyl acetal" is meant the reaction products of aldehydes with polyvinyl alcohol or a partially hydrolyzed polyvinyl ester under conditions suitable for the formation of an acetal.

The dye-forming polyvinyl acetals of this invention are conveniently prepared by the following general manner. One method comprises reacting polyvinyl alcohol under acetal-forming conditions 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, alkoxy, aryloxy, amino, alkylamino, arylamino, or mixed alkylaryl amino group. Other suitable aldehydes are those having active methylene groups.

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

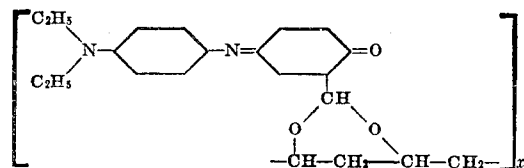
has the previously described structure. The methods are illustrated below.

These polymeric dye intermediates may be incorporated in a light sensitive emulsion and coated on a support by any of the general or known manners. After exposure, the intermediates are converted into dyes, for example, by development with a color-forming developer, such as p-aminodiethylaniline, or by some other suitable procedure such as a treatment with aromatic diazo compounds.

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 salicylaldehyde, 525 parts glacial acetic acid, and 5 parts 85% phosphoric acid were stirred and heated at 60-70° C. for nine hours. The translucent solution obtained was precipitated by addition of ethanol and water and washed successively with water and methanol. The yield of dry product amounted to 39 parts. This resin, when placed in a photographic 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 1 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 1 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 polyvinyl alcohol, 23 parts redistilled salicylaldehyde, 250 parts glacial acetic acid, and 2 parts 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 continued for three hours further. The resin was precipitated by addition of ethanol and water and washed successively with water and methanol. 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 an emulsion containing this product is coated on a suitable support, 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. Surprisingly, in view 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 polyvinyl alcohol, 250 parts glacial acetic acid, 23 parts salicylaldehyde, 9.4 parts phthalaldehydic acid, and 4 parts 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 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 emulsion sensitive only to blue light. After exposure and development with p-methylaminophenol 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 polyvinyl alcohol, 46 parts m-hydroxy-benzaldehyde, 500 parts glacial acetic acid, 18.4 parts phthalaldehydic acid, and 8 parts 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 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 polyvinyl alcohol, 84 parts glacial acetic acid, 8 parts o-nitrobenzaldehyde, 6 parts phthalaldehydic acid, and 3.2 parts 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 washed. It was then dissolved in dilute sodium hydroxide solution and reduced with sodium hydrosulfite. After neutralizing, the resin was precipitated with acetone, 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. After reprecipitating with acetone, washing, and drying, the product was introduced into a photographic emulsion which was subsequently coated on a cellulose acetate film, exposed and developed with p-aminodimethylaniline, a yellow dye being formed.

#### EXAMPLE VII

##### 2-hydroxy-3-methylbenzaldehyde

Twenty-two parts of polyvinyl alcohol was suspended in 250 parts glacial acetic acid. To this were added 15.5 parts 2-hydroxy-3-methyl-

benzaldehyde, 19 parts phthalaldehydic acid, and 4.3 parts 85% phosphoric acid and the mixture was heated on a water bath at 65° C. with vigorous stirring for 11 hours. At this time a thick translucent solution had formed. The resin was precipitated with methanol and washed in methanol and in water. Upon incorporation in an emulsion after the manner set forth in Example VI and subsequent development with p-aminodiethylaniline, a blue-green color formed.

#### EXAMPLE VIII

##### 3-chlor-2-hydroxybenzaldehyde

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 reaction was judged complete and the resin was precipitated and washed with methanol and water. Upon incorporation in an emulsion and after treatment as set forth in Example V, a blue-green color formed.

#### EXAMPLE IX

##### 5-chlor-2-hydroxybenzaldehyde

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 half hours heating at 65° C. was required to complete the reaction. The acetal was incorporated in an emulsion and treated after the manner set forth in Example VI, whereupon a blue-green color formed.

#### EXAMPLE X

Twenty-five parts 3-allyl-2-hydroxybenzaldehyde, 19 parts phthalaldehydic acid, 22 parts polyvinyl alcohol, 250 parts 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 this time a clear, homogeneous solution was obtained. The resin was precipitated by addition of methanol, redissolved in dioxan, and 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 emulsion, was found to yield a blue-green image after exposure and development with p-aminodiethylaniline.

#### EXAMPLE XI

Six parts 1-hydroxy-2-naphthaldehyde, 4 parts phthalaldehydic acid, 6.5 parts polyvinyl alcohol, 63 parts 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 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 emulsion, exposed, developed with metol-hydroquinone developer, bleached, re-exposed and developed with p-amino-diethylaniline, was found to yield a blue-green picture.

The term "polyvinyl alcohol" has been used herein to designate a substantially completely

hydrolyzed polyvinyl ester. The acetal formation may also be carried out upon a partially hydrolyzed polyvinyl ester. The acetals may also be conveniently prepared in one step from a polyvinyl ester by a simultaneous hydrolysis and acetalization. They may also be prepared from a mixture of aldehydes by simultaneous or stepwise reaction. An important modification of the process of acetal formation consists in using a process of acetal interchange. This is illustrated in the following example:

#### EXAMPLE XII

Nine parts polyvinyl alcohol, 15 parts salicylaldehyde, 6 parts of the diethyl acetal of glyoxylic acid, 105 parts glacial acetic acid and 6.8 parts of 85% phosphoric acid were stirred and heated together on a water bath at 65-70° C. for six hours. The viscous solution was precipitated by stirring in aqueous methanol and was then washed with water. After drying in air overnight the product was found to be soluble in dilute aqueous alkali and to yield a blue-green color upon development with oxidized p-aminodiethylaniline.

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-hydroxynaphthaldehyde, 3-dimethylaminobenzaldehyde, 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.

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, glyoxylic acid and propionaldehyde beta-sulfonic acid. In place of acetal formation with aldehydoacids, the acidic salt forming groups may also be introduced by any other suitable reaction such as

half-esterification with anhydrides of dibasic acids, such as phthalic or maleic anhydrides, or etherification with halogenated acids, such as 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-hydroxybenzaldehyde, 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 very 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, further reaction with the partially acetalized product may be carried out to give the polymer the desired properties. This further 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 aldehydes which may be used as modifying constituents for the acetals are formaldehyde, acetaldehyde, propionaldehyde, n- and iso-butylaldehyde, etc. Suitable cyclic ketones include cyclohexanone, 3-methyl cyclohexanone, 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 the 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 products of this invention are not limited in their utility to any one process of color photography. They may be used with other developing agents than those specifically described in the examples. The diamino aryl compounds such as para-phenylenediamine and its substitution products are preferred. 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 toluenylenediamines. The compounds, of course, must have one free or unsubstituted amine 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.

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 a number of the products are soluble in dilute alkali and certain of the processing solutions are alkaline in nature.

The dye forming polyvinyl acetals of this invention as well as the dyes are useful in other arts for color imparting purposes. They may be used in viscose dope as a coating composition. They may also be used for bringing up color in film by incorporation in viscose dope, coating a film from this composition and subsequent treatment with a diazo compound.

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 polyvinyl acetal formed from a polyvinyl alcohol and an aromatic aldehyde, said aldehyde

being capable of coupling with a diazo compound to form an azo dye.

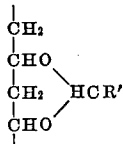
2. The acetals of carbonyl compounds containing a group capable of coupling with a diazo compound to form an azo dye with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups.

3. The acetals of aromatic aldehydes containing a group capable of coupling with a diazo compound to form an azo dye with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups.

4. The acetals of carbonyl compounds containing a group capable of coupling with a diazo compound to form an azo dye with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups, said acetals having further radicals containing free acid groups taken from the class consisting of carboxylic and sulfonic acid groups.

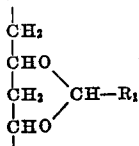
5. The mixed acetals of aromatic aldehydes containing a group capable of coupling with a diazo compound to form an azo dye, and aromatic aldehydes containing free carboxylic acid groups, with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups.

6. A polyvinyl acetal containing a plurality of groups having the structure:



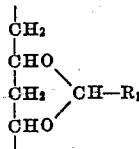
wherein R' is an aromatic hydrocarbon radical containing a phenolic hydroxyl group and having a reactive position in one of the positions taken from the group consisting of ortho and para to said hydroxyl group.

7. A polyvinyl acetal containing a plurality of groups having the structure:



wherein R<sub>1</sub> is a benzene nucleus containing a phenolic hydroxyl group and having a reactive position in one of the positions taken from the group consisting of ortho and para to said hydroxyl group.

8. A polyvinyl mixed acetal containing a plurality of groups having the structure:



wherein R<sub>1</sub> is an aromatic nucleus containing a phenolic hydroxyl group and having a reactive position in one of the positions taken from the group consisting of ortho and para to said hydroxyl group, and a plurality of acetal linkages of aldehydes containing free carboxylic acid groups.

9. The acetals of carbonyl compounds containing free carboxylic acid groups with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups, said compounds being solid, amorphous, high molecular products soluble in alkalies.

10. The acetals of aldehydes containing free carboxylic acid groups with compounds of the group consisting of polyvinyl alcohol and its derivatives containing free hydroxyl groups, said compounds being solid, amorphous, high molecular products soluble in alkalies.

11. The acetals of aldehydes containing a free carboxylic acid group with polyvinyl alcohol, said compounds being solid, amorphous, high molecular products soluble in alkalies.

12. The polyvinyl acetal of salicylaldehyde with polyvinyl alcohol.

13. The polyvinyl mixed acetal of 5-chloro-2-hydroxy-benzaldehyde and phthaldehydic acid with polyvinyl alcohol.

14. The polyvinyl mixed acetal of salicylaldehyde and phthaldehydic acid with polyvinyl alcohol.

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