

UNITED STATES PATENT OFFICE

2,551,133

PHOTOGRAPHIC LIGHT-SENSITIVE DIAZO
ELEMENT

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8 Claims. (Cl. 95-7)

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This invention relates to photography and, more particularly, to light-sensitive photographic elements containing light-sensitive diazonium salts and to compositions and preparing the same. Still more particularly it relates to photographic elements comprising a support bearing a hydrophilic color former layer having intimately dispersed therethrough light-sensitive diazonium salts and to processes for making such layers.

An object of this invention is to provide a new type of light-sensitive photographic element. A more specific object is to provide such an element which contains light-sensitive diazonium salts. A further object is to provide such an element which may be processed rapidly to yield reproductions of high contrast with good resolving power and definition. A still further object is to provide a simple and economical method for preparing such elements. Still other objects will be apparent from the following description of the invention.

The novel photographic elements of this invention consist of a support which bears at least one water-permeable layer composed of a hydrophilic, polymeric color former which has intimately dispersed therethrough light-sensitive diazonium salts. The hydrophilic, polymeric color formers consist of synthetic, organic, polymeric compounds which contain a polymeric chain nucleus and include in their molecular structure nuclei which are capable of forming azomethine or indophenol dyes on color coupling development of exposed silver halides. These color formers are also capable of coupling with diazo compounds to form diazo dyes. Hence when light-sensitive diazonium salts are incorporated with them, the latter compounds couple under the conditions suitable for development of light-sensitive diazonium salts to form polymeric azo dyes.

The novel elements consist essentially of two components, namely, the hydrophilic, polymeric color former and the light-sensitive diazonium salt. Hence they are quite simple to fabricate and process. The coating techniques for preparing the emulsions or light-sensitive coatings are simplified by reason of the two-component nature of the final product.

The coating solutions may be prepared by dissolving the hydrophilic, polymeric color former and light-sensitive diazonium compound in a

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suitable solvent or mixture of solvents, such as methanol, ethanol, dioxane, etc., and mixtures of such solvents with water. The hydrophilic, polymeric color former and the light-sensitive diazonium compound may be dissolved in the same solution by adding them separately or simultaneously or they may be separately dissolved in different portions of the same solvent and admixed with stirring. Stabilizing agents for the diazonium salts can be incorporated with the coating solutions if desired. The resulting solutions may then be applied to a support to form a thin layer and dried. The preparation of the solutions and the coating operations should, of course, be carried out in the absence of actinic radiations which would affect the light-sensitive diazonium compounds.

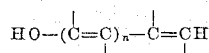
An alternative method of preparing the light-sensitive coatings or layers is to dissolve the hydrophilic, polymeric color former in a solution and to coat this upon a support to form a layer which is then dried. The dried layer is then impregnated with a solution containing the light-sensitive diazonium compound. The latter solution freely permeates throughout the entire layer and as it dries it deposits the light-sensitive salt uniformly throughout the layer.

In the preferred form of the invention there are used hydrophilic hydroxyl color formers which consist of a linear polymer chain which has attached, to recurring carbon atoms thereof, a hydroxyl group and, to other recurring carbon atoms, color former nuclei capable of forming azomethine or indophenol dyes through a covalent bond. The color former nuclei may be attached to recurring carbon atoms of the polymer chain through ether or acetal linkages. The hydrophilic hydroxyl color former polymeric polymers, in general, should contain at least one aliphatic hydroxyl group to every eight carbon atoms in the chain, i. e., 12.5 hydroxyl groups to every 100 chain atoms, and preferably one to two hydroxyl groups for every five chain atoms, i. e., between 25 and 50 hydroxyl groups for every 100 chain atoms. The color former nuclei or radicals are attached to the polymeric chain either directly or indirectly and it is preferred that for every 100 chain atoms there be present between one and 35 color former nuclei. These preferred hydrophilic, hydroxyl polymer color

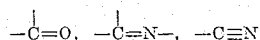
formers, moreover, should have a polymer chain containing more than 200 carbon atoms.

Suitable synthetic hydroxyl polymers that may be connected to color forming nuclei to produce the hydrophilic color forming hydroxyl polymers of the present invention include hydrolyzed polyvinyl esters, i. e., polyvinyl alcohols, hydrolyzed interpolymers of vinyl esters, e. g., vinyl acetate, vinyl propionate, and vinyl butyrate, etc., with olefins, e. g., ethylene, propylene, butene-1, and other vinyl compounds, e. g., acrylic acid, acrylic acid alkyl esters, alkyl methacrylates, vinyl chloride, vinyl cyanide, and maleic anhydride, and also the partial esters, ethers, and acetals of such polymers. These polymers may be connected to the color former nuclei by various chemical groupings or linkages, such as, for example, carbonamide, sulfonamide, amino groups, acetal, ester, ether linkages, etc.

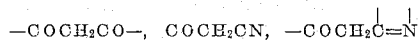
The color former nuclei or components of the above synthetic polymers have as active coupling groups a structure which may be represented as



where n is 0 or 1. This structure is found in color formers which contain a reactive acyclic or intracyclic methylene group and in aromatic hydroxyl compounds. These groups occur in phenols (including naphthols), acylacetarilides, cyanoacetarilides, beta-keto-esters, pyrazolones, N-homophthalylamines, coumaranones, indoxyls, thioindoxyls, etc. The reactive groups may also be termed reactive methylene, reactive ethenol, and reactive 4-hydroxy-1-3-butadienyl groups. These reactive methylene groups have a hydrogen rendered mobile by the proximity of certain unsaturated groups, such as, for example



and others. The $-\text{CH}_2-$ group is usually present between two such groups, for example,



in a cyclic or acyclic system. In all of the color former nuclei the hydrogen atoms in the coupling position may be replaced by groups which are readily eliminated in the coupling reaction, e. g., halogen, e. g., chlorine and bromine, sulfonic acid, carboxylic acid, etc.

Suitable specific color formers of the above type are described in United States Patents 2,310,943, 2,320,422, 2,397,864, and 2,397,865.

The coating solutions described above may be applied to the support by any of the conventional coating procedures, e. g., by dipping, spraying, coating from hoppers by means of beading rollers, etc. They may be applied to practically any type of support, such as metal, plastic, glass, transparent film base, water-proofed paper, cellulose derivatives, superpolymers, e. g., nylon, etc.

The invention will be further illustrated by the following examples.

Example I

A 5% solution of meta(1-hydroxynaphthalene-2-sulfoamido)benzaldehyde polyvinyl acetal (prepared as described in application Serial Number 667,111, filed May 3, 1946, now U. S. Patent No. 2,423,572) was prepared in a water-ethanol solution containing 75 parts of the former and 25 parts of the latter by weight. The resulting solution was deposited on a baryta coated paper support at a coating weight of 60 milligrams per square decimeter of said acetal.

The resulting layer was dried at a temperature of about 40–50° C. in a current of air. A 2% solution of the zinc double salt of diazotized p-amino-diethylaniline in water was supplied to the layer. The entire operation was carried out in the absence of actinic light. The resulting element, after drying, was exposed to a positive transparent image by means of a 500 watt 3200° K. lamp at a distance of three feet for ten minutes. The exposed element was subsequently developed by fuming it with ammonia vapor for a period of ten minutes. A strong, positive image, which was brown in color, was formed.

Example II

A 5% solution of meta(p-15-ethylcarbonato-3-methyl - 1 - pyrazoyl)benzamido]benzaldehyde acetal of polyvinyl alcohol (prepared as described in application Serial Number 667,126, filed May 8, 1946, now U. S. Patent No. 2,476,988) was substituted for the acetal of Example I. The resulting element was exposed and developed as described in that example whereby a magenta image was formed.

Example III

A 5% solution of meta(benzoylacetamido)benzaldehyde polyvinyl acetal (prepared as described in application Serial Number 667,126, filed May 3, 1946, now U. S. Patent No. 2,464,597) was substituted for the acetal of Example I. The resulting element was exposed and processed as described in that example and a strong, orange image was obtained.

In place of the specific color formers of the above examples, there may be substituted other hydrophilic polymeric color formers and especially those of the aforementioned patents with similar results.

Any organic solvent or mixture of solvents may be employed in preparing the solutions as long as they are not reactive with the diazo compounds. Thus ketones, such as acetone, methyl ethyl ketone, cyclohexanone, etc., cannot be used, while alcohols, e. g., methanol, ethanol, n-propanol, isopropanol, n-butanol, secondary butanol, etc.; glycols, e. g., ethylene glycol, diethylene glycol, propylene glycol; ethylene glycol monomethyl and monoethyl ethers; ethylene glycol dimethyl ether; tetrahydrofuran; esters, e. g., methyl acetate, ethyl acetate, ethyl propionate, ethyl butyrate, ethyl glycolate, ethyl methoxyacetate; hydrocarbons, e. g., hexane, benzene; chlorinated hydrocarbons, e. g., chloroform, carbon tetrachloride, ethylene dichloride, etc., can be used providing that they are solvents for all the constituents of the coating composition.

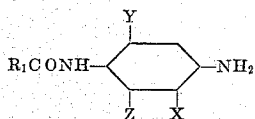
The preferred solvents or solvent solutions are those which are water-miscible to the extent that 10% or more water can be dissolved therein. A small amount of water in the coating composition is desirable and aids in dissolving the diazonium compound and in securing an even light-sensitive coating. Further, it is usually desirable to use those with an appreciable vapor pressure at normal temperatures so that drying times will be as short as possible. However, in addition, portions (e. g., 5 to 25%) of solvent with a higher vapor pressure, e. g., boiling between 100° and 200° C., are advantageous as an aid in securing even flow-outs and smooth coatings.

In preparing solutions for application by spraying, it is often desirable to add an anti-foaming agent, e. g., long chain aliphatic alcohol, e. g.,

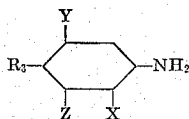
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decyl, dodecyl, tetradecyl, etc., so that an even coating free from bubbles may be obtained.

Other light-sensitive diazo compounds than those of the above examples may be employed. The more commonly used diazo compounds include those prepared from the following amines:



and



where R_1 and R_2 are organic radicals, e.g., aromatic hydrocarbon, aliphatic hydrocarbon, heterocyclic, etc.; also R_1 and R_2 may together form a saturated, unsaturated, or heterocyclic ring. R_3 may be the same as R_1 or may be $-\text{SR}_1$, $-\text{OR}_1$, $-\text{NHCOOR}_1$, $-\text{NHCONHR}_1$. X and Y may be H, Cl, Br, alkyl, aryl, alkoxy, aryloxy, halogenoalkyl, etc. Z is hydrogen or, together with X , may form an aromatic or heterocyclic ring. Specific compounds of this type include p - aminoacetanilide, p - aminobenzanilide, 4 - amino-2,5-dimethoxyacetanilide; 4-amino-2, 5-dichlorobenzanilide; 1-amino - 4 - acetaminonaphthalene; 4-aminodiethylaniline, 4-aminodimethylaniline; 4-amino-2-methyldiethylaniline; N(p-aminophenyl)morpholine; N(4-amino-2,5-diethoxyphenyl)piperidine; 1-amino-4-dimethylaminonaphthalene, 4-amino-diphenyl, 4-aminocarboethoxyaniline; methyl, 4 - amino-2,5-dimethoxyphenyl urea; phenyl, 4-amino-2,5-dichlorophenyl urea.

Any of the various known sensitizers, such as urea, thiourea, allyl thiourea, thiosulfate, etc., and/or compounds which form double salts with diazonium compounds, such as tin, zinc, or cadmium salts, of weak acids, e. g., tartaric, citric, succinic, boric, etc., may be employed in these compositions. The latter compounds prevent coupling prior to exposure.

It is also desirable in some cases to add pigments to the compositions. For instance, if the light-sensitive composition is to be applied to a surface which is dark in color or unpainted and it is desired to have the maximum contrast, a pigment is added which is complementary in color to that of the final azo dye produced in the drawing. Thus, if the dye formed is black, a white pigment may be added, such as titanium dioxide or barium sulfate pigment. If the final colors are to be red, a green pigment may be used, or if they are to be blue, a yellow pigment may be used or any other such combination.

Suitable diazo stabilizers which prevent decomposition of the light-sensitive diazonium compounds when coated on metal plates, e. g., ferrous metal plates, are metal deactivators and corrosion inhibitors which are unreactive toward diazonium salts. Compounds useful for this purpose include water-soluble metal nitrites, e. g., alkali metal nitrites, alkyl nitrites, e. g., amyl nitrite; alkyl phosphates, e. g., monododecyl phosphate, didodecyl phosphate; and aromatic phosphates, e. g., tricresyl phosphate. These compounds may be used in small amounts, e. g., 0.01 to 0.2% based on the total weight of the hydrophilic, polymeric color former used.

Self-supporting foils may be made by coating the hydrophilic, polymeric color former solu-

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tions onto a smooth surface, drying the resulting film element, and stripping it from the casting surface.

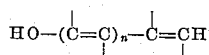
The light-sensitive, hydrophilic, polymeric color former coating compositions hereof have the advantage that they form water-permeable layers which are free from tackiness so that the surface will not stick to other materials, even when stored in a humid place. The resulting layers have a tough, smooth surface and are not softened by water sufficiently to cause scratching or marring when handled wet.

The coating compositions of this invention have a wide utility and are generally useful where it is desired to copy a design, drawing, lettering, plan, etc., onto any water-resistant surface. Thus, in the manufacture of templates for use in preparing parts of machinery, airplanes, boats, automobiles, electrical equipment, etc., the materials to be used, such as metal, composition boards, etc., are coated with the light-sensitive compositions of this invention, dried, exposed through the master drawing, and developed. The finished print, which adheres firmly and is an exact duplicate of the original, is used to cut out the template. Stencils or lettered transparencies may also be used to reproduce directions, identification numbers, etc., on parts or finished articles of manufacture. Elements may also be prepared by coating the light-sensitive solutions on flexible bases, such as film base, water-proofed paper, plastic sheeting, and the like. Such elements may be used to prepare permanent records or may be fastened adhesively to permanent supports, e. g., metal, boards, etc.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

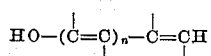
What is claimed is:

1. Photographic element comprising a support bearing at least one layer composed of a hydrophilic polymeric color former having light-sensitive diazonium compounds uniformly dispersed therethrough, said color former containing a multiplicity of recurring active groups which have a structure represented by the formula



where n is a number taken from the group consisting of 0 and 1.

2. Photographic element comprising a support bearing at least one layer composed of a hydrophilic polymeric color former having light-sensitive diazonium salts uniformly dispersed therethrough, said color former containing a multiplicity of recurring active groups which have a structure represented by the formula

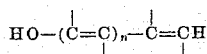


where n is a number taken from the group consisting of 0 and 1.

3. Photographic element comprising a support bearing at least one layer composed of a hydrophilic hydroxyl polymer color former having light-sensitive diazonium salts uniformly dispersed therethrough, said color former containing a multiplicity of recurring $-\text{CH}_2-\text{CHOH}-$ groups and a multiplicity of recurring active

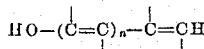
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groups which have a structure represented by the formula



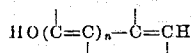
where n is a number taken from the group consisting of 0 and 1.

4. Photographic element comprising a support bearing at least one layer composed of a hydrophilic polyvinyl acetal color former which contains a multiplicity of recurring $\text{CH}_2-\text{CHOH}-$ groups and a multiplicity of recurring active groups which have a structure represented by the formula



where n is a number taken from the group consisting of 0 and 1, the color former nuclei being linked to the chain atoms of said polymer through an acetal linkage having light-sensitive diazonium salts uniformly dispersed there-through.

5. A photographic element comprising a water-proofed paper support bearing a layer composed of a hydrophilic polyvinyl alcohol acetal color former having light-sensitive diazonium compound uniformly dispersed therethrough, said polyvinyl acetal color former containing a multiplicity of recurring extralinear active groups which have a structure represented by the formula



where n is a number taken from the group consisting of 0 and 1.

6. A photographic element comprising a water-proofed paper support bearing a layer composed of m - (1-hydroxynaphthalene-2-sulfonamido) - benzaldehyde polyvinyl acetal having a zinc double salt of diazotized p -aminodiethyl aniline uniformly dispersed therethrough.

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7. A photographic element comprising a water-proofed paper support bearing a layer composed of m -(p -[5-ethylcarbonato-3-methyl-1 - pyrazoyl]benzamido) benzaldehyde polyvinyl acetal having a zinc double salt of diazotized p -aminodiethyl aniline uniformly dispersed therethrough.

8. A photographic element comprising a water-proofed paper support bearing a layer composed of m -(benzoylacetamido) benzaldehyde polyvinyl acetal having a zinc double salt of diazotized p -aminodiethyl aniline uniformly dispersed there-through.

ANDREW BRADSHAW JENNINGS.
OTIS WILLARD MURRAY.

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