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2,405,523

LIGHT-SENSITIVE PHOTOGRAPHIC COMPOSITIONS AND ELEMENTS

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This invention relates to photography and, more particularly, to light-sensitive photographic elements and to their preparation. Still more particularly, it relates to water-resistant supports bearing a water-permeable layer composed of a vinyl resin binder containing a light-sensitive diazonium salt, and to compositions for making such layers.

An object of this invention is to provide new and useful light-sensitive diazo salt solutions which are stable, of low water content, and can be coated to form smooth, tough, mar-resistant surfaces. A related object is to provide such solutions which are fast drying, not softened by water, and have good adherence to water-resistant surfaces. A further object is to provide photographic elements with water-insoluble but water-permeable, light-sensitive layers which may be processed rapidly to yield reproductions of high contrast, resolving power, and definition. Still other objects will be apparent from the following description of the invention.

The above objects are attained by the preparation and use of the novel coating compositions, layers and photographic elements described below. The coating solutions in their broader aspects consist of a solvent containing a water-permeable, water-insoluble resinous lower aliphatic ester or acetal of a vinyl alcohol polymer which acts as a binding agent or medium for a light-sensitive diazonium compound. The novel light-sensitive layers and elements contain or comprise a stratum composed essentially of the aforesaid resinous ester or acetal and the diazonium salt. The solvent is completely or substantially removed during a coating operation. Since organic solvents may be used, the drying time may be greatly reduced. However, a small amount of water may be present in the solvent mixture to aid in dissolving the diazonium compound.

In a preferred aspect of the invention the coating composition layers and elements further contain a stabilizing agent for the light-sensitive diazonium compound. This may advantageously be introduced during the preparation of the coating composition but may be added just prior to coating if desired.

The coating solutions may be prepared by dissolving the polyvinyl ester or acetal and light-sensitive diazo compound in a suitable solvent or mixture of solvents, such as methanol, ethanol, dioxane, etc. The polyvinyl ester or acetal and diazo compound may be dissolved in the same solution separately or dissolved in different portions of the same solvent and admixed with stir-

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ring, if desired. The stabilizing agent can be added in like manner. The solutions may then be applied to a support and the resulting layers dried. The preparation of the solutions and coating operations should, of course, be carried out in the absence of actinic radiations which would affect the light-sensitive diazo compounds.

The coupling components, e. g., phenols, naphthols, reactive methylene compounds, etc., used to form the final dye image in the layer may be incorporated with the coating solutions in the same manner as the diazo compound. The development of the resulting elements may be carried out after exposure by treatment with ammonia vapor or an alkaline solution. On the other hand, the elements which are free from coupling components may be treated, after exposure, in an alkaline developer solution containing the coupling components.

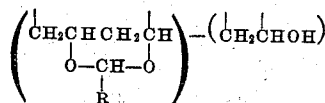
The preferred resinous lower aliphatic acetals and esters of vinyl alcohol polymers used in accordance with the teachings hereof have the following properties.

(A) They are soluble to the extent of at least 5% and preferably 10% in an organic solvent system which will dissolve the light-sensitive diazo compound without reaction therewith and are insoluble in water even when warmed to 80° C.

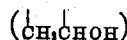
(B) They are permeable to aqueous processing solutions, i. e., they have a water absorption of at least 10% which permits rapid processing after exposure. The term "water absorption of 10%" means that an unsupported film about 0.002 inch thick which has been dried at 60° C. for 24 hours and placed in water at normal temperatures (20-25° C.) for one-half hour will absorb water equivalent to 10% of its weight.

(C) They have a softening point above 60° C. when dry.

The preferred resins having these properties are prepared by (1) polymerizing vinyl acetate or vinyl propionate to such an extent that a solution of 86 g. of the polymer in 1000 cc. of benzene has a viscosity of between 50 and 150 centipoises; or (2) acetalizing polyvinyl alcohol (viscosity of 4% aqueous solution at 20° C. being between 10 and 50 centipoises) to give a polymer represented by the formula:



wherein the



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radical represents approximately 25 to 40% of the total weight of the polymer and R is CH_3 —; CH_3CH_2 —; $\text{CH}_3\text{CH}_2\text{CH}_2$ —; or $(\text{CH}_3)_2\text{CH}$ —.

These coating compositions are applied by dipping, painting or spraying onto water-resistant surfaces such as metals, plastics, composition boards, glass, transparent film base, water-proofed paper, cellulose, or the like. After coating, the surface will dry in the air or may be warmed to 40 to 50° C. in a current of air to speed drying. Higher temperatures however are often injurious to the light-sensitive compound. The final element is then ready for use or may be stored for periods up to several months before use.

Heretofore it has been impossible to apply diazonium compounds directly to ordinary untreated iron and steel surfaces which are not corrosion-resistant since a rapid interaction occurs between the metal and diazonium salt. This results in formation of rust and decomposition of the diazo salt. Now it has been found, and this is an important feature of the present invention, that when certain diazo stabilizers are added to the light-sensitive solutions they may be applied directly to iron and steel surfaces without the necessity of applying a separate overcoat to the metal. As a result, such new coating compositions have a much wider utility than those previously described. Suitable diazo stabilizers which prevent decomposition of the diazonium compounds 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., mololuryl phosphate, dilaurylphosphate, aromatic phosphates, e. g., tricresylphosphate. These compounds are required in only very small amounts, i. e., 0.01 to 0.2% based on the total weight of binder used. When a soluble stabilizer such as sodium nitrite is used and a wet processing step employed, it is desirable to add a small amount of the stabilizer to the final wash. Metal deactivators that contain amino groups are not practical in this process since they react with the diazo compound themselves.

The following examples, in which all parts are by weight, are further illustrative of the nature of the invention. In the preparation and coating of these light-sensitive diazonium solutions all light is excluded which will decompose the diazonium compounds.

Example I

Twenty-seven parts of p-aminodiethylaniline sulfate is dissolved in 100 parts of water containing 12.5 parts of concentrated hydrochloric acid and cooled to 0° C. To this is added 20 parts of 5 molar sodium nitrite solution at -5° C. After five minutes 20 parts of zinc chloride is added and the solution stirred while adding 30 parts of sodium chloride at 5° C. The resulting crystalline product, the zinc chloride double salt of p-diethylaminobenzene diazonium chloride, is removed by filtration and washed with 10% sodium chloride solution and dried by suction for ten minutes. Eighteen parts of this moist diazo salt is dissolved in 80 parts of 95% ethanol, filtered, and mixed with 320 parts of a solution prepared by dissolving 100 parts of polyvinyl acetate (viscosity 85-115 centipoises at 20° C. of a solution of 86 g. in 1000 cc. of benzene measured in a Hoeppler viscometer; melting range 180-200° C.) in 500 parts of 95% ethanol

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and the solution diluted with ethanol to 800 parts and used as a stock solution.

Example II

Glass, aluminum, stainless steel, and painted (alcohol-resistant lacquer) steel plates are dipped in a mixture of 100 parts of the stock solution of Example I and 100 parts of ethyl acetate. The coating dries in about 5 minutes at 50° C. and the resulting plates are ready for use. When ordinary steel plates are used in place of the above supports either (A) two parts of 10% sodium nitrite or (B) one part of 10% sodium nitrite and two parts of 1% dilauryl phosphate in ethanol is added to the coating solution of Example I before dipping to prevent destruction of the diazo salt. The dried plates are placed under a film containing a line drawing and exposed to sunlight for 15 seconds, then developed in a solution prepared by dissolving the ingredients in the following order:

	Parts
Water	300
Sodium hydroxide	5
Sodium sulfite	10
Sodium thiosulfate	40
Ethanol	80
2,3-hydroxynaphtholic anilide	5
Alpha-naphthol	0.3
Water to make	1,000

To this solution is added 5 parts of activated charcoal and the mixture filtered to yield a clear, pale yellow solution. The plates, after being immersed in this developing solution for 30 seconds, followed by washing in water and drying, contained a positive reproduction of the original drawing with sharp, grainless black lines. The surfaces are smooth, hard, and mar-resistant.

Example III

To a solution containing 10 parts of polyvinyl acetate of the type described in Example I dissolved in 195 parts of ethanol, 25 parts of ethyl acetate, 20 parts of butyl acetate, and 20 parts of β -ethoxyethanol there is added 10 parts of the diazo salt of Example I. Using a brush, this solution is spread evenly on metal surfaces, e. g., aluminum, stainless steel, painted steel. In five minutes the coating has set, and after drying for 15 minutes at 40° C. a smooth even coating of the light-sensitive composition is ready for exposure and development as in Example II.

Example IV

To a solution of 10 parts of polyvinyl acetate (as described in Example I) in 155 parts of ethanol, 80 parts of ethyl acetate, 50 parts of butyl acetate, 25 parts of β -ethoxyethanol, and 2 parts of octyl alcohol is added 8 parts of the diazo salt of Example I. This solution is placed in a paint sprayer and sprayed under 40 pounds pressure onto aluminum and painted steel plates. After drying 15 minutes, at 40° C., smooth, even, light-sensitive coatings are obtained and the plates are used as in Example II.

Example V

In place of the polyvinyl acetate of Examples I, II, III and IV is used a polyvinyl acetaldehyde acetal prepared by acetalizing 65% of the hydroxyl groups of a completely hydrolyzed polyvinyl alcohol which has a viscosity of 18-28 centipoises (4% aqueous solution at 20° C.). Similar results are obtained.

This invention is not limited to the use of the

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specific resins of the above examples, but other specific ester or acetal resinous vinyl alcohol polymers having the general properties as heretofore defined may be employed. The following list exemplifies other suitable resinous polymers that may be employed:

Polyvinyl acetate or propionate less than 50% hydrolyzed.

Interpolymers of vinyl acetate or vinyl propionate with terminally unsaturated mono-olefins, e. g., ethylene having an olefin content between about 2 and 40% which are not more than 50% hydrolyzed.

Interpolymers of vinyl acetate with minor (mol ratio less than 1) parts of other unsaturated compounds, e. g., vinyl chloride, vinylidene compounds, alkyl acrylates, alkylmethacrylates, etc., which are not more than 50% hydrolyzed.

Polyvinyl alcohol and completely hydrolyzed interpolymers of vinyl acetate with less than 40% of an unsaturated polymerizable compound, e. g., mono-olefins, such as ethylene, vinyl chloride, alkyl acrylates, etc., which have been condensed with lower aliphatic aldehydes, e. g., $\text{CH}_3(\text{CH}_2)_n\text{CHO}$ where $n=0$ to 2 to form acetal groups on between about 40 and 80% of the hydroxyl groups.

Plasticizers though usually unnecessary may be used in the polyvinyl resinous esters, if desired. Suitable plasticizers including dibutyl sebacate, methylphthalate, methyl glycolate, N-ethyl-p-toluene-sulfonamide and dimethoxymethyl adipate may increase the flexibility of the resins. In general, they should be used in a small amount, e. g., 1 to 10% by weight based on the amount of polyvinyl ester.

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, iso-propanol, n-butanol, secondary butanol, etc., glycols, e. g., ethylene glycol, diethylene glycol, propylene glycol, ethylene glycol monomethyl and ethyl ethers; ethers, e. g., 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.

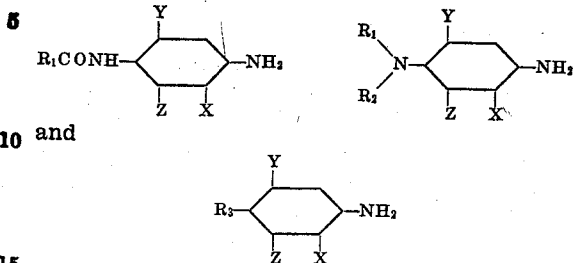
The preferred solvents or solvent solutions are those which are water miscible to the extent that 10% or more water can be dissolved therein. A small amount of water in the coating composition is desirable and aids in dissolving the diazonium compound and in securing an even light-sensitive coating. 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., 5-25%) 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., decyl, dodecyl, tetradecyl, etc., so that an even coating free from bubbles may be obtained.

Other light-sensitive diazo compounds than

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



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-aminobenzoacetanilide, 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-dimethylnaphthalene; 4-aminodiphenyl; 4-aminocarbomethoxyaniline; 4-amino-2,5-dimethoxyphenyl urea; 4-amino-2,5-dichlorophenylurea.

The light-sensitive solutions of this invention in general have a solids content, e. g., diazo plus binder, of between about 1 and 20%. However, it has been found that the best coatings are obtained with solutions in the range of about 2 to 7% solids content, depending upon the particular resin employed and the method used in applying the solution. Thus, for brushing or dipping, higher solids contents may be employed, while for spraying it is usually desirable to use a more dilute solution containing a higher percentage of a solvent with a boiling point about 100° C. In general, it has been found that the best results are obtained when the ratio of diazo to binder is in the order of about 1:1 to 1:3, although in certain cases a higher or lower ratio may be useful.

Other coupling components than those of the above examples may be employed. They are, in general, phenols and naphthols, typical of which are the following:

Di- and trihydric phenols, e. g., resorcinol, phloroglucinol
 Alpha-naphthol and beta-naphthol
 1-naphthol-3,8-disulfonic acid
 1-naphthol-4,7-disulfonic acid
 1,8-Dihydroxynaphthalene-3,6-disulfonic acid
 2,7-Dihydroxynaphthalene
 2-naphthol-6,8-disulphonic acid
 Acetoacetanilide and its substitution products
 Phenylmethylpyrazolone and its substitution products
 Amides of 2-hydroxy-3-naphthoic acid, e. g., the anilide, 3-methylanilide, alpha-naphthylamide, beta-naphthylamide, and 4-phenylanilide.

Although aromatic amino coupling components cannot be added to the light-sensitive solutions since they react to form dyes even in acidic solu-

tion, they may be employed in the developer solution. Such compounds include anilines, naphthylamines, aminophenols and aminonaphthols unsubstituted or having substituents in the ring or in the amino group, e. g., o-toluidine, m-aminophenol, 1-amino-8-naphthol-3,6-disulfonic acid.

In addition, the compositions of this invention can be prepared by use of the appropriate diazos for use according to the Frangialli process (see French Patent No. 853,868 and United States Patent No. 2,313,288) wherein the surface is exposed to a strong ultraviolet source, i. e., a carbon light which destroys the diazo in the transparent portions of the drawing. The drawing is then removed and the light-sensitive surface moistened and exposed to a light of low ultraviolet intensity for a short period. This causes a conversion of a part of the diazo to a phenol and is followed by coupling with the unconverted diazo to form a dye image.

Positive prints can also be obtained directly from negatives by the use of diazo sulfonates such as described in United States Patents 2,197,456 and 2,217,189. In addition, the process of United States Patents 2,034,508 and 2,067,690, wherein diazo compounds are converted to the colored oxidation products of phenols under the influence of light, can be applied to the present invention.

Any of the other types of light-sensitive diazos, including those capable of self-coupling, such as are prepared from aminonaphthols, can be employed in the present invention by using the appropriate processing steps.

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.

The light-sensitive coating compositions hereof have the advantages that they form water-permeable layers which are (a) not softened by water sufficiently to cause scratching or marring when handled wet, (b) resistant to dilute acids and alkalis at least for a short time, (c) capable of forming tough, strong, unsupported coherent films, having a tensile strength greater than 1000 lb./sq. in. when dry or wet, and are free from brittleness which will cause chipping or flaking

when the support is cut or trimmed, and (d) free from tackiness so that the surface, when stored in a humid place will not stick to other materials.

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, waterproofed 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.

What is claimed is:

1. A coating composition comprising a water-miscible organic solvent having dissolved therein a water-insoluble resinous polyvinyl acetate free from hydroxyl groups and having a water absorption of at least 10%, a light-sensitive diazonium salt, a diazo stabilizer, taken from the group consisting of water-soluble alkali metal nitrites, alkyl nitrites, and hydrocarbon phosphates, a diazo coupling component, and not more than 10% of water.

2. A coating composition comprising a mixture of ethanol and ethyl acetate having dissolved therein a water-insoluble resinous polyvinyl acetate which is free from hydroxyl groups and has a water absorption of at least 10%, from 0.01 to 0.2% of sodium nitrite based on the weight of said polyvinyl acetate, a light-sensitive diazonium salt, and not more than 10% of water.

3. A photographic element comprising a ferrous metal support bearing a layer comprising a water-insoluble resinous polyvinyl acetate free from hydroxyl groups and having a water-absorption of at least 10% which has intimately dispersed therethrough a light-sensitive diazonium salt, a diazo stabilizer taken from the group consisting of water-soluble alkali metal nitrites, alkyl nitrites, and hydrocarbon phosphates, and a diazo coupling component.

4. A photographic element comprising a ferrous metal support bearing a layer comprising a water-insoluble resinous polyvinyl acetate free from hydroxyl groups and having a water-absorption of at least 10% which has intimately dispersed therethrough a light-sensitive diazonium salt and from 0.01 to 0.2% of sodium nitrite based on the weight of said polyvinyl acetate.

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