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LIGHT-SENSITIVE LAYERS OF N-MONOARYLHYDROXYLAMINES AND THEIR NITRONES AND PROCESS OF PRINTING THEREON

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7 Claims. (Cl. 95—7)

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This invention relates to photography. More particularly, it relates to light-sensitive elements for obtaining direct prints. Still more particularly, it relates to photographic elements which contain light-sensitive N - monoarylhydroxylamines and their nitrones and to processes of obtaining prints therefrom.

Various light-sensitive materials have been used for the preparation of photographic images or prints. A widely used photographic printing material, however, has as the light-sensitive component a photographic silver halide emulsion in a colloid layer. These elements are exposed to an object and then developed in a developer solution and finally the undeveloped silver salts are removed, leaving a negative metallic silver image. Other light-sensitive elements have utilized the light-sensitive dichromates and light-sensitive diazonium salts. The latter materials, after exposure to an image, are developed by treatment with a basic solution of a coupling component such as a naphthol. In the latter case, however, a positive image results since the diazo compound is destroyed in the exposed areas and rendered incapable of coupling. The above described photographic elements, while very useful, have some disadvantages. In the first place, the light-sensitive silver halides are quite expensive. The light-sensitive dichromates result in images of somewhat inferior quality and require a rather tedious processing.

An object of this invention is to supply a new type of photographic material which is free from the disadvantages of the previously proposed materials. A further object is to provide an economical photographic printing element. Another object is to provide a new method of producing photographic prints. Still other objects are to provide a new use for N-monoarylhydroxylamines and their nitrones and to provide a general advance in the art of photography.

The above objects are attained by the preparation and use of photographic elements which have a radiation-sensitive layer composed of an N-monoarylhydroxylamine or a nitrone thereof. The elements may be prepared by coating a support with a thin layer of an N-monoarylhydroxylamine or a nitrone thereof dispersed in a hydrophilic colloid medium. For example, an N-monoarylhydroxylamine, e. g., N-phenyl, N-p-tolyl, or N-alpha-naphthylhyroxylamine, or a nitrone thereof, is incorporated in an aqueous solution of a water-permeable colloid such as gelatin and coated on to a support such as paper, metal, glass, or a transparent film base such as a cellulose derivative or a synthetic resin or a superpolymer, e. g., nylon. The N-monoarylhydroxylamines are prepared and coated in the absence of actinic radiations.

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The element containing the N-monoarylhydroxylamine or nitrone is exposed through a photographic element containing an image by means of actinic light whereby there is formed in the first named element an image which has a density gradation complementary to the image in the second element. The image formed may be fixed by simply removing the undeveloped portion by washing in a solvent for the hydroxylamine or nitrone, e. g., an aqueous solution.

The N-monoarylhydroxylamines and their nitrones are especially sensitive to ultraviolet light and it is preferable to use as a source of actinic light a source which is rich in wave lengths of light in the ultraviolet light region of the spectrum. Suitable sources include sunlight, arc lights, including carbon arcs and metal or metal salt-cored carbon arcs, mercury vapor lamps, rare gas lamps, and fluorescent lamps.

The nitrones comprehended by the invention are the condensation products of N-monoarylhydroxylamines with aldehydes and ketones. The condensation apparently takes place in accordance with the equation:

$$ArNHOH + R_1R_2CO \longrightarrow R_1R_2C{=}N{-}Ar + H_2O$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow O$$

In this equation R_1 and R_2 are hydrogen or a hydrocarbon radical which may be aliphatic, aromatic, aliphatic-aromatic, cyclo-aliphatic, or a heterocyclic radical and Ar is an aryl group. The nitrones have greater chemical stability than the N-monoarylhydroxylamines.

The invention will be further illustrated, but is not intended to be limited, by the following examples wherein the parts are by weight unless otherwise indicated and all procedures prior to exposure are carried out in the absence of actinic light:

Example 1

A solution of one part of N-alpha-naphthylhydroxylamine in 10 parts of methanol is coated on paper and allowed to dry. The resulting light-sensitive element is exposed through a negative photograph with ultraviolet light having wave lengths from 3000 to 4000 Å. for a period of 60 seconds, whereby a red positive image appears on the surface of the coated paper. The resulting print is washed in the water to remove the unexposed and colorless material and a red posi-

tive image having gradations complementary to that of the negative photograph is obtained.

Example 2

A solution containing one part on N-alpha-naphthylhydroxylamine in 10 parts of methanol was added to a solution of 10 parts of gelatin in 90 parts of water containing about 0.05 parts of sodium dodecyl sulfate. This solution was coated onto a cellulose acetate film base and dried. The element thus formed is exposed under a photographic film element containing a negative silver image to a carbon arc for 120 seconds, and a red positive image forms in the element. The film is washed in water to remove the unexposed and colorless materials, whereby a red positive picture image results which has gradations complementary to the silver image of the original negative.

Example 3

In place of the specific hydroxylamine of Example 2 is substituted one part of N-p-tolylhydroxylamine and a photographic element is made and processed in the same manner. A yellow image is formed.

Example 4

A solution containing 5 parts of alpha-phenyl-N-p-tolylnitrone (obtained by condensing benzaldehyde with N-p-tolylhydroxylamine) in 95 parts of methanol-water is coated on an opaque paper base and dried. The element is exposed through a photographic element containing a negative picture image in the form of metallic silver for 60 seconds to the ultraviolet light of a mercury arc whereby a yellow positive image is formed. The paper was washed in a solution of warm water to remove the unexposed colorless nitrone.

Example 5

A solution of 5 parts of alpha-phenyl-N-phenylnitrone (obtained by condensing N-phenylhydroxylamine with benzaldehyde) in 150 parts of ethanol is coated onto an opaque paper base and then dried. A photographic element containing a negative picture image is placed on the paper element and exposed to the ultraviolet light of a mercury arc for 60 seconds, whereby a yellow-brown positive image is formed. After washing the paper in warm water a yellow-brown picture remains which has gradations complementary to that in the original negative.

In place of the specific N-monoarylhydroxylamines and nitrones in the above examples, there may be substituted other of such compounds. Suitable additional materials include N-phenylhydroxylamine, N-o-tolylhydroxylamine, N-p-tolylhydroxylamine, N-o-chlorophenylhydroxylamine, N-(4-dimethylamino-alpha-naphthyl) hydroxylamine, N-alpha-naphthylhydroxylamine, N-xenylhydroxylamine, N-beta-naphthylhydroxylamine, N-p-methoxyphenylhydroxylamine, N-2,4-dimethoxyphenylhydroxylamine, N-2,4-dimethylphenylhydroxylamine.

The N-monoarylhydroxylamines are somewhat unstable when subjected to elevated temperatures or prolonged storage at moderate temperatures or to humid conditions. The nitrones, however, are more stable under these conditions. Moreover, the light-sensitivity of the nitrones varies over a greater wave length range than that of the corresponding N-monoarylhydroxylamines. Thus, by merely varying the aldehyde or ketone used to condense with the N-monoarylhydroxylamine one may obtain products which have a wide range of sensitivity to light. For example, alpha-phenyl-N-phenylnitrone is sensitive only to wave lengths of light below about 3000 Å., whereas alpha-furyl-N-phenylnitrone has a sensitivity extending into the visible spectrum. On the other hand, the N-monoarylhydroxylamines appear to be somewhat more sensitive to actinic light than their nitrones. The nitrones need not be preformed but can be formed in situ. Thus a mixture of N-hydroxylamines and an aldehyde or ketone of the types herein disclosed can be separately incorporated in the light-sensitive layers, or in the coating compositions just prior to coating.

A wide variety of aldehydic and ketonic compounds (ketaldones) may be reacted with the N-monoarylhydroxylamines to produce the light-sensitive nitrones. Among the useful aldehydes are benzaldehyde, p-tolualdehyde, cinnamaldehyde, furfural, benzaldehyde-o-sodium sulfonate, sodium phthalaldehydate, sodium glyoxylate, o-chlorobenzaldehyde, phenylacetaldehyde, acetaldehyde, acrolein, methacrolein and crotonaldehyde. Suitable ketonic compounds include acetone, methyl ethyl ketone, diethyl ketone, diamyl ketone, methyl n-butyl ketone, acetophenone, levulinic acid, sodium levulinate, ethyl acetoacetate, ketobutanol, methyl vinyl ketone, and benzophenone. Aldehydes and ketones which contain the group

$$-\overset{|}{C}=\overset{|}{C}-$$

are preferred, since the resulting compounds are more sensitive to ultraviolet light.

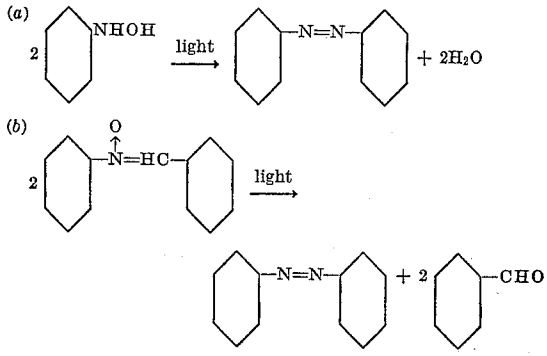
Variations in the effective wave length of the elements can be obtained by varying the particular hydroxylamine or its nitrone used. Thus, N-alpha-hydroxylnaphthylamine is sensitive to longer wave lengths than N-p-tolylhydroxylamine which is, in turn, affected by light which is of longer wave length than that to which N-phenylhydroxylamine is sensitive. Mixtures of the compounds can be employed, thus resulting in a product which is sensitive over a fairly wide range of wave length of light.

The N-monoarylhydroxylamines and their nitrones can be made into photographic layers by applying them from solutions in various organic solvents or water dispersions. Practically any organic solvent may be employed in preparing the solutions, so long as it does not react with the N-monoarylhydroxylamines or nitrones. Useful solvents include alcohols of 1 to 4 carbon atoms, e. g., methanol, ethanol, isopropanol, butanol; glycols, e. g., ethylene glycol, diethylene glycol; ethers, e. g., dioxane, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether; esters, such as ethyl acetate, methyl acetate, etc.; hydrocarbons, e. g., n-hexane, n-heptane, benzine, tetrahydronaphthalene, cyclohexane, benzene, ortho-meta- and para-xylenes, ethyl benzene, mesitylene, chloroform, ethylene dichloride, trichloroethylene, etc. It is preferred to use water-miscible solvents, however, such as the alcohols of 1 to 4 carbon atoms.

Dispersions of the N-monoarylhydroxylamines and their nitrones in various water-permeable or various hydrophilic colloids may be obtained by simply dissolving the compounds in an alcohol and mixing them with an aqueous solution of the colloid. Suitable colloids include gelatin, casein, zein, deacylated chitin, polyvinyl alcohol and its hydrophilic derivatives, gum tragacanth, agar-agar, Irish moss, ethyl cellulose, polymethacrylamide, cellulose acetate containing 20 to 25% of acid phthalate groups, etc. The resulting solu-

tions or dispersions may be coated onto any type of support, as described above, and dried. In general, it is preferred to have the compounds dispersed in a colloid layer because they are more stable and can be stored at elevated temperatures for several weeks without suffering any loss of sensitivity. Gelatin in particular has a stabilizing influence upon the compounds. In general, from 0.001 to 0.1 part of the N-monoarylhydroxylamine or nitrone should be used per part of gelatin. Layers of various thicknesses can be used but, for most purposes, thicknesses of from one to ten microns are suitable. It is not necessary that the colloid layer be highly permeable to water since cellulose esters, e. g., cellulose acetate and vinyl resins, e. g., polyvinyl acetate, can be used.

The nature of the reaction which takes place when the compounds are exposed to actinic light is not fully understood. It is believed, however, that the images produced upon exposure (*a*) of the N-monoarylhydroxylamines and (*b*) the N-arylnitrones are symmetrical azo dyes in accordance with the following exemplary respective equations:



The formation of azo dyes may explain the fact that yellow images are produced from N-phenylhydroxylamine and red from N-alpha-napthylhydroxylamine. Based on the assumption that symmetrical azo dyes are formed, it is theoretically possible to produce any color dye image which can be derived from a symmetrical azo dye. This fact may be of utility in connection with certain processes of color photography. For example, a layer containing three nitrones capable of giving yellow, magenta and blue-green azo dyes could be printed with three separation negatives successively, in register, limiting the printing light to that portion of the spectrum to which only the desired nitrone is sensitive.

The compounds differ in the speed with which image formation takes place and this fact may sometimes be advantageous. For example, the benzaldehyde and furfuraldehyde derivatives of N-phenylhydroxylamine are much more rapidly decomposed by ultraviolet light than the salicylaldehyde and the cinnamaldehyde reaction products.

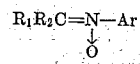
The light-sensitive elements of this invention may be used in many types of copying processes since exposure through a negative yields a positive image in the new element, which may be used for the preparation of "proofs" or as permanent photographic prints. Their ease of processing to colored images makes them especially applicable to the reproduction of line drawings, charts, etc., as an improvement over photostating or blueprinting from papers, etc., and in the production of templates.

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 the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

What is claimed is:

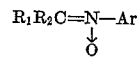
1. A radiation-sensitive element comprising a support bearing a water-permeable colloid layer containing an N-arylnitrone.

2. A radiation-sensitive element comprising a support bearing a water-permeable colloid layer containing at least one compound taken from the group consisting of N-monoarylhydroxylamines of the formula ArNHOH and their nitrones of the formula



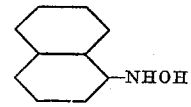
wherein Ar is a monovalent aromatic hydrocarbon nucleus and R_1 and R_2 are taken from the group consisting of hydrogen and monovalent hydrocarbon radicals.

3. A radiation-sensitive element comprising a support bearing a gelatin layer containing at least one compound taken from the group consisting of N-monoarylhydroxylamines of the formula ArNHOH and their nitrones of the formula

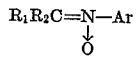


wherein Ar is a monovalent aromatic hydrocarbon nucleus and R_1 and R_2 are taken from the group consisting of hydrogen and monovalvent hydrocarbon radicals.

4. A radiation-sensitive element comprising a paper support bearing a layer of gelatin containing N-alpha-naphthylhydroxylamine of the formula:

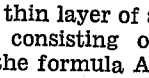


5. The process which comprises printing a photographic image by means of light rays onto a radiation-sensitive element comprising a support bearing a thin layer of a compound taken from the group consisting of N-monoarylhydroxylamines of the formula ArNHOH and their nitrones of the formula



wherein Ar is a monovalent aromatic hydrocarbon nucleus and R_1 and R_2 are taken from the group consisting of hydrogen and monovalent hydrocarbon radicals, and washing the undeveloped colorless compound just recited from the layer with an aqueous solution.

6. The process which comprises printing a photographic image by means of light rays onto a radiation-sensitive element comprising a paper support bearing a thin layer of a compound taken from the group consisting of N-monoarylhydroxylamines of the formula ArNHOH and their nitrones of the formula



wherein Ar is a monovalent aromatic hydrocarbon nucleus and R_1 and R_2 are taken from the group consisting of hydrogen and monovalent hydrocarbon radicals, and washing the undeveloped colorless compound just recited from the layer with an aqueous solution.

7. The process which comprises printing a photographic image by means of light rays onto a radiation-sensitive element comprising a paper support bearing a water-permeable colloid layer containing a compound taken from the group consisting of N-monoarylhydroxylamines of the formula ArNHOH and their nitrones of the formula

$$R_1R_2C{=}N{-}Ar \rightarrow O$$

wherein Ar is a monovalent aromatic hydrocarbon nucleus and R_1 and R_2 are taken from the group consisting of hydrogen and monovalent hydrocarbon radicals, and washing the undeveloped colorless compound just recited from the layer with an aqueous solution.

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The following references are of record in the file of this patent:

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Number	Name	Date
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