United States Patent

DeMeyer et al.

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[54] LIGHT SENSITIVE HALOCARBON AND PHENOL DERIVATIVE COMPOSITION

[72] Inventors: **Dennis E. DeMeyer,** Rochester, N.Y.; **Frank D. Allen, deceased,** late of Rochester, N.Y. by Mona Armstrong Allen executrix, Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

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[52] **U.S. Cl.** **96/48,** 96/90

[51] **Int. Cl.** **G03c 5/24,** G03c 1/72

[58] **Field of Search** 96/90, 48

[56] **References Cited**

UNITED STATES PATENTS

3,490,907 1/1970 Schenck et al. 96/90

Primary Examiner—Norman G. Torchin
Assistant Examiner—Richard E. Fichter
Attorney—W. H. J. Kline, J. R. Frederick and D. M. De Leo

[57] **ABSTRACT**

Photographic elements having a support on which is coated a layer including a light-sensitive halocarbon and a phenol derivative like 1-naphthol, pyrocatechol or 1-methoxy-2-naphthol, yield printout images on exposure to actinic rays. The printout image can be intensified by heating.

6 Claims, No Drawings

LIGHT-SENSITIVE HALOCARBON AND PHENOL DERIVATIVE COMPOSITION

This invention relates to photography and particularly to photographic elements and processes for forming printout images.

It is known that polyhalocarbons are light-sensitive and yield photographic products which are capable of producing colored materials from such colorless materials as certain dyes, and diarylamines. Examples of this light-sensitivity can be found in Mechanisms and Structures In Organic Reaction, Gould, page 744; and in U.S. Pat. No. 3,102,810 and 3,121,633; in British Pat. Nos. 916,779 and 719,919. These references are based on the photoreaction of polyhalocarbons with leuco dyes to yield the corresponding colored forms of the dyes.

While polyhalocarbons have been employed separately as light-sensitive addenda for certain photographic processes and elements they have not been combined with phenol derivatives to prepare photographic printout elements.

Accordingly, an object of this inventor is to provide novel photographic elements.

Another object of this invention is to provide new photographic elements useful in preparing printout images.

Still another object of the present invention is to provide novel photographic elements including, as the image-forming components, at least one polyhalocarbon and at least one phenol derivative.

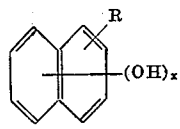
An additional object of this invention is to provide a new photographic process for producing printout images.

Other objects and advantages of this invention will become increasingly apparent from a reading of the following specification and appended claims.

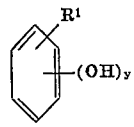
The objects of this invention are accomplished both with photographic elements wherein a support is coated with a layer including a light-sensitive halocarbon and a phenol derivative and with a photographic process for the preparation of printout images including imagewise exposing an element such as described above.

Phenol derivatives useful in the photographic element of this invention are generally mono-and polycyclic aromatic phenol compounds including mono-and polyhydroxylic compounds which can be additionally substituted with, for example, alkyl radicals, alkoxy radicals and the like which themselves can be either unsubstituted or substituted.

Especially advantageous phenol derivatives include those having the formulas

I 

and

II 

wherein:

a. each of R and R^1 represents a member which is either a hydrogen atom, an alkyl radical or an alkoxy radical, and

b. each of *x* and *y* represents a positive integer having a value of from 1 to 3

As defined herein, the term alkyl radical refers to straight and branched chain alkyl radicals having from one to about eight carbon atoms like methyl, ethyl, 2-methoxyethyl, propyl, isopropyl, n-butyl, n-hexyl, n-heptyl, n-octyl, etc. The term alkoxy radical refers to alkoxy radicals having from one to about eight carbon atoms such as methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, octoxy and the like. Preferably, the alkyl and alkoxy radicals used herein have from one to four carbon atoms.

Exemplary phenol derivatives include such compounds as:

1-naphthol,
2-naphthol,
1,3-naphthalenediol,
2,3-naphthalenediol,
2,7-naphthalenediol,
4,5-naphthalenediol,
1,5-naphthalenediol,
1,4-naphthalenediol,
1-methoxy-2-naphthol,
2-ethyl-1,8-naphthalenediol,
1-pentoxy-2,7-naphthalenediol
pyrocatechol,
4-n-butoxypyrocatechol,
5-methylpyrocatechol
4-n-pentylresorcinol, phloroglucinol, and
4-n-hexylresorcinol

Also included in the present photographic elements, in combination with at least one phenol derivative like those mentioned hereinabove is at least one halocarbon or polyhalocarbon compound. The phenols and halocarbon compounds are generally combined herein in weight ratios of from about 3:1 to 1:5 respectively, and preferably in substantially equal amounts by weight. Useful halocarbon compounds include, for example, γ-halocarbonyl compounds like γ,γ,γ-tribromoacetophenone, poly(vinylhalides) such as poly(vinyl bromide) as well as perhalide and the like. Especially desirable halocarbon compounds are those known to be decomposed by exposure to actinic rays (i.e., ultraviolet and blue light) and which are not acidic. Preferred halocarbon compounds of this type include polyhalocarbons having three halogen atoms chemically bonded to a terminal carbon atom, i.e., those having the formula:

$$R^2—C—(X)_3$$

wherein X represents a halogen atom and R^2 represents either a halogen atom, an alkyl radical, a haloalkyl radical, an aryl radical or an aroyl radical. Exemplary polyhalocarbons include such compounds as polyhaloalkanes like iodoform, carbon terabromide, pentabromoethane, hexabromoethane, hexachloroethane and tribromophenylmethane.

Bromo and iodo compounds are especially preferred due to their inherently greater light-sensitivity as compared to that of the corresponding chloro compounds. Polyhalocarbons, such as iodoform, which can be inactivated or diffused from a coated layer on heat treatment are also preferred since they permit convenient stabilization of the photographic image by the application of heat.

In addition to phenol derivatives and halo-carbon compounds, the photographic elements of this invention can contain additional addenda e.g., sensitizers, or addenda to enhance either image quality of raw stock or image stability. As an example, certain nitrogen containing compounds promote the photographic speed and resultant image density at any given exposure level. These materials are well known in the photographic art and include such compounds as 5-dimethylaminocoumarin, 6-diethylamino-4-methylcoumarin, carbazole, diphenylformamide, 4-dimethyl-aminobenzaldehyde, phenothiazine and the like.

As well as sensitizing addenda, materials which exhibit premature reaction in the sensitive layers are useful inclusions. Presumably, such compounds, which can be included singly or in combination and admixture, function to buffer the image-forming components against a pH change, i.e., to an acidic pH, which would promote a premature printout reaction. Desirable stabilizing materials include nitrogen-containing heterocycles like benzimidazole, 2-methylbenzimidazole, 2-styrylbenzimidazole as well as related nitrogen containing compounds such as azoles like isazole, triazole, benzotriazole, etc.; azure compounds like pyrimidine, pyrazine, benzopyrimidine, and other diazines or triazine compounds such as 1,2,4-triazine, 1,2,3-triazine, 1,3,5-triazine, etc.

Other useful addenda materials include image stabilizers, they being compounds which enhance the resistance of a resilient photographic image against deterioration from subsequent exposure to heat, light or the like energies which can cause fading or discoloration of the image. Exemplary such stabilizers include thiazine compounds like phenothiazine and oxines such as alkoxyboraxines.

Generally, the image-forming components and additional stabilizing or other modifying addenda are dispersed in a hydrophobic film-forming resin binder to promote the forma-

tion of a coated layer. Desirable resinous matrix vehicles include those which have a softening point sufficiently high to resist tackiness at the temperature ranges, i.e., up to about 150° C., useful for intensifying photographic images produced on elements of this invention. Additionally, the pH of the resin binder should not be such that it either promotes or unduly inhibits, i.e., more than do the described stabilizers, the image-forming reaction. Exemplary matrix vehicles, having the noted characteristics, can be selected from a wide variety of materials, including natural resins, modified natural resins and synthetic resins. Exemplary useful natural resins are balsam resins, colophony and shellac. Exemplary suitable modified natural resins are colophony-modified phenol resins and other resins listed below with a large proportion of colophony. Suitable synthetic resins include the extensive variety of synthetic resins, for example, polymers, such as vinyl polymers including polyvinyl chloride, polyvinylidene chloride, polyvinyl acetate, polyvinyl acetals, polyvinyl ether and polyacrylic and polymethacrylic esters; polystyrene and substituted polystyrenes or polycondensates, e.g., polyesters, such as phthalate resin, terephthalic and isophthalic polyesters, maleinate resin and colophony-mixed esters of higher alcohols; phenol-formaldehyde resins, including colophony-modified phenol-formaldehyde condensates, aldehyde resins, ketone resins, polyamides and polyadducts, e.g. polyurethanes. Moreover, high-melting polyolefins, such as various polyethylenes, polypropylenes, polyisobutylenes, and chlorinated rubber are suitable. Additional useful resinous binder materials are known to those skilled in the polymer arts.

To prepare a composite photographic element of this invention, the image-forming components and such supplemental addenda compounds are desired are generally dissolved or dispersed in a solution of matrix vehicle to prepare a coating composition which can then be applied to a support material by solvent coating techniques. In a coating formulation, the polyhalocarbon and phenol derivative are generally present in stoichiometric amounts or with an excess of phenolic compound. Modifying addenda if included, can be present in widely varying amounts and the chosen amount will depend on both the selection and quantities of image-forming components as well as the modifying effect desired. Conventionally they are included in an amount of from about 1 to 10 percent of weight of the image-forming ingredients, although higher concentrations can be used if desired. The image-forming compositions, including stabilizers or other modifying addenda, are generally incorportated into a coating formulation in an amount of from about 5 to about 50 parts by weight per 100 parts by weight of matrix vehicle. Advantageously, the composite coating formulation contains from about 5 to about 20 weight percent solids for ease of coating, although wider variations can be used if desired for particular situations.

Coating can be accomplished by a wide variety of techniques including flow coating, doctor blade coating, whirl coating, extrusion hopper coating, etc. The support material onto which the light-sensitive layer is applied is widely variable and includes such supports as cellulosic materials like cellulose acetate, cellulose acetate butyrate, etc., as well as polystyrenes, polycarbonates, polyvinyl compounds like polyvinylacetals, polyesters such as poly(ethylene terephthalate), polyy-olefins like polyethylene, polypropylene and other polyy-olefins conventionally having from two–10 carbon atoms, and including metals like zinc and aluminum and paper including polyethylene and polypropylene coated papers.

After coating and drying to form a composite photographic element of this invention, the resultant element can be imagewise exposed to actinic rays to prepare visible printout images. After exposure, heating like that previously described can be employed to intensify or stabilize the light induced photographic image. Stabilization, as noted above, is accomplished by exhausting unreacted halocarbon from the layer. Intensification results from the heat promoted action of an image intensifier like those described herein. Desirably, heating is within range of from about 100° C. to about 150° C., but wider variations in temperature can be used if desired.

The following examples are included for a further understanding of the invention:

EXAMPLE 1

A coating composition including 0.1 g. 4-methoxy-1-naphthol and 0.1 g. carbon tetrabromide in 1 ml. of dichloroethane is added to 4 ml. of a 10 percent benzene solution of a styrene-butyl methacrylate copolymer is doctor blade coated at a wet thickness of 0.004 inches on paper support and allowed to dry. The dry coating is then exposed to actinic rays through a line negative transparency on the exposure unit of an Ozamatic Printer at a linear speed of 5 ft./in. The exposed element is then heated for ten seconds at 150° C. in order to stabilize the print against further light reaction. The printout image is brownish-yellow in exposed areas on a white background.

EXAMPLE 2

A coating solution including 0.1 g. phloroglucinol and 0.1 g. iodoform in 1 ml. of dichloroethane is added to 4 ml. of a 10 percent solution of poly(vinyl-butyral) in a five to one mixture of dichloroethane and methanol. The composition is then coated on poly(ethylene terephthalate) support at a wet thickness of 0.004 inch as in Example 1 and allowed to dry. The resultant element is exposed and heated as in Example 1 to obtain a bright yellow image on a clear background.

EXAMPLE 3

A coating composition as in Example 2, except employing pyrocatechol as the color-forming agent, is doctor blade coated at a wet thickness of 0.004 inch on a like support and allowed to dry. The dry coating is exposed and heated as in Example 1 to give a brown image on a clear background.

EXAMPLE 2

A coating composition identical to that in Example 2, except employing resorcinol as the dye-forming agent, is similarly coated at a wet thickness of 0.004 inch on a similar support and allowed to dry. The dried coating is exposed and heated as in Example 1 to give a light orange image on a clear background.

EXAMPLE 5

A coating composition employing 2,3-naphthalenediol as the color-forming agent, but otherwise identical to that in Example 2, is similarly coated on a like support at a wet thickness of 0.004 inch and allowed to dry. The dry coating is exposed and heated as in EXample 1 to give a brown image on a clear background.

EXAMPLE 6

A coating composition as in Example 2 but employing 2,7-naphthalenediol as the dye-forming agent is doctor blade coated at a wet thickness of 0.004 inch on Estar film base and allowed to dry. The dry coating is then exposed and heated as in Example 1 to give a brownish-orange image on a clear background.

EXAMPLE 7

A coating composition employing 1,5-naphthalenediol as the color-forming agent, but otherwise identical to that in Example 2, is doctor blade coated at a wet thickness of 0.004 inch on poly(ethylene terephthalate) support and allowed to dry. The resultant element is exposed and heated as in Example 1 to give a brown image on a light yellow background.

EXAMPLE 8

A coating composition as in Example 2, except employing 1-naphthol as the dye-forming agent, is doctor blade coated at a wet thickness of 0.004 inch on poly (ethylene terephthalate) support and allowed to dry. The resultant element is exposed and heated as in Example 1 to give a gray image on a clear background.

EXAMPLE 9

A coating composition identical to that in Example 2, except employing 2-naphthol as the color-forming agent, is doctor blade coated on poly(ethylene terephthalate) support at a wet thickness of 0.004 inch and allowed to dry. The element is then exposed and heated as in Example 1 to produce a brown image on a clear background.

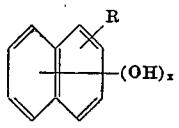
EXAMPLE 10

A coating composition containing 4-hexylresorcinol as the color-forming agent, but otherwise identical to that in Example 2, is doctor blade coated at a wet thickness of 0.004 inch on Estar film base and allowed to dry. The resultant element is exposed and heated as in Example 1 to provide a light orange image on a clear background.

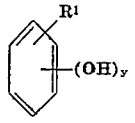
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. A photographic element for the production of printout images and comprising a support having coated thereon a layer comprising a light-sensitive polyhalocarbon compound and a phenol derivative having a formula selected from:



and



wherein:

a. each of R and R^1 represents a member selected from the group consisting of a hydrogen atom, an alkyl radical and an alkoxy radical, and

b. each of x and y represents a positive integer having a value of from 1 to 3, said phenol and said halocarbon being combined in a weight ratio of from 3:1 to 1:5 respectively.

2. A photographic element as described in claim 1 wherein each of the alkyl and alkoxy radicals represented by R and R^1 has from one to four carbon atoms.

3. A photographic element as described in claim 1 wherein the phenol derivative is selected from the group consisting of:

a. 1-naphthol
b. 2-naphthol
c. 2,3-naphthalenediol
d. 2.7-naphthalenediol
e. 1,5-naphthalenediol
f. 1-methoxy-2-naphthol
g. pyrocatechol
h. resorcinol
i. phloroglucinol
j. 4-n-hexylresorcinol

4. A photographic element for the production of printout images and comprising a support having coated thereon a layer comprising a light-sensitive polyhalocarbon selected from the group consisting of carbon tetrabromide and iodoform and a phenol derivative selected from the group consisting of 4-methoxy-1-naphthol, phloroglucinol, resorcinol, 2,3-naphthalenediol, 2,7-naphthalenediol, 1,5-naphthalenediol, 1-naphthol, 2-naphthol and 4-n-hexylresorcinol, said phenol and said halocarbon being combined in a weight ratio of from 3:1 to 1:5 respectively.

5. A photographic image-forming process for the preparation of printout images on a photographic element as described in claim 1, which process comprises imagewise exposing said element to actinic rays whereupon a printout image is produced in exposed areas.

6. A photographic process as described in claim 5 and additionally including heating said exposed element to intensifying the printout image.

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