

1

3,597,212

PHOTOSENSITIVE ELEMENTS AND PROCESS

Frank G. Webster and Donald W. Heseltine, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y.

No Drawing. Filed Oct. 30, 1968, Ser. No. 772,020

Int. Cl. G03c 1/52; B41m 5/00

U.S. Cl. 96—90

16 Claims

ABSTRACT OF THE DISCLOSURE

Photosensitive elements and a process of photographic reproduction are described employing a photosensitive composition comprising a heterocyclic nitrogen compound and a ketomethylene compound or a reactive cyclic ammonium quaternary salt which on exposure to actinic radiation react to form a dye.

This invention relates to photographic reproduction of images and to radiation sensitive compositions and elements useful for photographic reproduction. In a particular aspect it relates to radiation sensitive compositions and elements for copying images by a dry process.

Many compounds and compositions are known which are useful for the reproduction of images by photographic means. Photographic systems are known in which photo-exposure produces either a visible or a latent image by such means as the photo-reduction of a heavy metal salt, such as silver halide; the photoinduced reaction between a colorless pair of compounds to give a colored reaction product; the photobleaching of a colored compound to a colorless form; the photopolymerization of an unsaturated monomer to a polymer; the photocrosslinking of a polymer to a hardened form; etc. Despite this wide variety of photographic materials, each of these systems has certain advantages and certain drawbacks which makes them useful for some types of photographic reproduction and disadvantageous for other types of photographic reproduction. Thus, there is a continual search for new photosensitive compounds and compositions which will combine in a single system a maximum of the advantages associated with different prior art photographic systems while minimizing their disadvantages.

Accordingly, it is an object of this invention to provide novel photographic compositions and elements.

It is another object of this invention to provide novel photographic elements in which an image is formed directly upon exposure to light without need for further development.

It is yet another object of this invention to provide a novel dry photographic system which obviates the need for liquid chemical development.

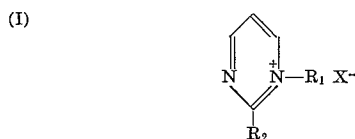
It is still another object of this invention to provide a dry process for producing photographic images using the novel photographic compositions and elements of this invention.

The above and other objects of this invention will become apparent to those skilled in the art from the further description of the invention which follows.

In accordance with the present invention, we have found that photosensitive elements can be prepared from a photosensitive composition comprising as a first component a salt of a heterocyclic nitrogen compound and as a second component a ketomethylene dye precursor compound or a reactive cyclic ammonium quaternary salt. By the term reactive cyclic ammonium quaternary salt we mean a cyclic ammonium quaternary salt which contains in the heterocyclic ring an active methylene group adjacent the nitrogen atom. Upon exposure to actinic radiation these two components react to form a colored dye in exposed areas.

2

The heterocyclic nitrogen compounds which are useful in the practice of this invention include pyrimidinium salts having the structural formula



and pyridinium salts having the structural formula

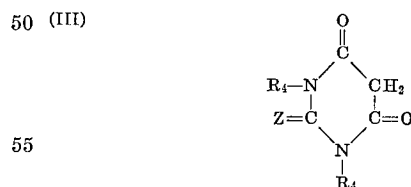


wherein R_1 and R_3 are independently a hydrogen atom, an alkyl group typically having 1 to 12 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tertiary butyl, hexyl, octyl, decyl, etc.) including substituted alkyl groups (e.g., benzyl, phenylpropyl, etc.) or an aryl group typically having 1 to 2 rings (e.g., phenyl, tolyl, naphthyl, etc.); R_2 is a hydrogen atom, a halogen atom, a substituted or unsubstituted alkyl group or aryl group, as defined above for R_1 and R_3 , or an amino group; and X^- is an anion such as an acetate ion, a sulfate ion, a p-toluenesulfonate ion, a tetrafluoroborate ion, a halogen ion, etc.

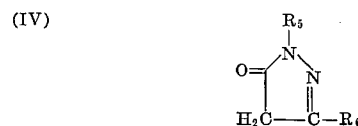
Typical heterocyclic nitrogen compounds which are useful in the practice of this invention are

pyridinium acetate,
pyridinium p-toluenesulfonate,
pyridinium chloride,
1-methylpyridinium acetate,
1-ethylpyridinium p-toluenesulfonate,
1-phenylpyridinium acetate,
1-benzylpyridinium tetrafluoroborate,
pyrimidinium acetate,
pyrimidinium p-toluenesulfonate,
1-methylpyrimidinium acetate,
1,2-diethylpyrimidinium p-toluenesulfonate,
2-ethyl-1-phenylpyrimidinium tetrafluoroborate,
2-chloro-1-ethylpyrimidinium acetate,
2-amino-1-methylpyrimidinium p-toluenesulfonate, etc.

The ketomethylene compounds which are useful in the photosensitive compositions of the present invention include barbituric acids having the structural formula

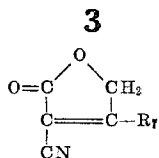


wherein Z is an oxygen or a sulfur atom, and each R_4 is independently a substituted or unsubstituted alkyl group or an aryl group, as defined above; 2-pyrazolin-5-ones having the structural formula



wherein R_5 is a hydrogen atom, a substituted or unsubstituted alkyl group or an aryl group, as defined above and R_6 is a substituted or unsubstituted alkyl group or an aryl group, as defined above; and 3-cyano-2(5H)-furanones having the structural formula

(V)



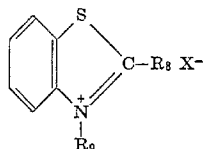
wherein R_7 is a substituted or unsubstituted alkyl group or an aryl group, as defined above. These furanone compounds and the method of their preparation are more fully described in copending patent application of J. A. Ford and C. V. Wilson U.S. Ser. No. 555,239, filed June 6, 1966, now U.S. Pat. No. 3,468,912 issued Sept. 23, 1969.

Typical of the ketomethylene compounds which are useful in the practice of this invention are

1,3-diethylbarbituric acid,
1,3-dibutylbarbituric acid,
1,3-diphenylbarbituric acid,
3-benzyl-1-phenylbarbituric acid,
1,3-diethyl-2-thiobarbituric acid,
1,3-diphenyl-2-thiobarbituric acid,
1,3-dibenzyl-2-thiobarbituric acid,
1,3-diethyl-2-pyrazolin-5-one,
1,3-diphenyl-2-pyrazolin-5-one,
3-methyl-1-phenyl-2-pyrazolin-5-one,
3-benzyl-1-ethyl-2-pyrazolin-5-one,
3-cyano-4-methyl-2(5H)-furanone,
3-cyano-4-ethyl-2(5H)-furanone,
3-cyano-4-phenyl-2(5H)-furanone,
4-benzyl-3-cyano-2(5H)-furanone, etc.

Typical reactive cyclic ammonium quaternary salts, which are useful in the practice of this invention are the benzothiazolium salts having the structural formula

(VI)



where R_8 and R_9 are each an alkyl group typically having 1 to 8 carbon atoms (e.g., methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, amyl, hexyl, octyl, etc.); and X^- is an anion as defined above. Representative benzothiazolium salts include 2,3-dimethylbenzothiazolium p-toluenesulfonate, 2,3-diethylbenzothiazolium acetate, 3-ethyl-2-methylbenzothiazolium p-toluenesulfonate, 3-butyl-2-ethylbenzothiazolium tetrafluoroborate, etc.

Upon exposure to actinic radiation the compositions of this invention undergo a change in photoexposed areas from a colorless or pale colored form to an intensely colored dye. While we do not wish to be bound by any particular theory as to the reason or mechanism for the dye formation, it is believed that upon exposure to actinic radiation the heterocyclic nitrogen compound cleaves giving a reactive intermediate which supplies the polymethine chain to join two of the ketomethylene or reactive cyclic ammonium quaternary salt moieties to form a dye.

Photographic elements employing the photosensitive compositions of this invention can be prepared by methods conventional in the art. The photosensitive composition can be imbibed into an absorbent support, or an absorbent material coated on a base support, it can be incorporated in a binder which is then coated on a base support, or it can be incorporated in a self-supporting binder.

The photosensitive compositions of this invention preferably employ a molar excess of the ketomethylene or reactive cyclic ammonium quaternary salt component. Preferably, for each part of the heterocyclic nitrogen component in the composition, there is employed from two to ten parts of the ketomethylene or reactive cyclic ammonium quaternary salt component.

Suitable absorbent supports include fibrous materials

4

such as paper, cloth, parchment, etc., ceramic materials, gelatin, synthetic polymers such as poly(vinyl alcohols), poly(vinyl phthalates), carboxymethyl cellulose, cellulose ether phthalates, copolymers of alkyl acrylates with acrylic acid, etc., and the like. The wearing and handling properties and the dimensional stability of elements prepared with these absorbent materials can be improved by coating certain of them, e.g., gelatin and the polymeric materials, on such non-absorbent base supports as metal sheets and foils, polyester film base, e.g., poly(ethylene terephthalate) film, poly(ethylene sebacate) film, poly(ethylene adipate) film, etc., cellulose ester film base, e.g., cellulose nitrate film, cellulose acetate film, cellulose acetate-butyrate film, cellulose acetate-propionate film, etc., and the like.

The photosensitive composition is imbibed into the absorbent support by contacting the support with a solution of the reactive components in a solvent therefor such as water, an alkanol, e.g., methanol, ethanol, isopropanol, etc., or the like. The solution can be swabbed or sprayed onto the surface of the absorbent support or the support can be immersed into the solution. The two reactive components need not be imbibed into the support at the same time. The support can be first contacted with a solution of one of the reactive components and then subsequently the other reactive component can be imbibed into the support.

Binders in which the photosensitive reactants of this invention can be incorporated to form a coating composition include such film-forming vehicles as gelatin, olefinic polymers, such as polyethylene, polystyrene, butadiene-styrene copolymers, poly(ethylene oxides), poly(vinyl chloride), poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride-acetate), poly(ethylene-vinyl acetate), poly(vinyl acetals), copolymers of vinylidene chloride with such monomers as vinyl acetate, acrylonitrile, and ethyl acrylate, and polyacrylate and methacrylate esters such as poly(ethyl acrylate) and poly(butyl methacrylate); polyesters and copolyesters of glycols and dibasic acids such as terephthalic, isophthalic, sebacic and adipic acids; cellulose esters, such as cellulose acetate, and cellulose acetate-butyrate; and cellulose ethers such as methoxyethyl cellulose.

A coating composition for preparing photosensitive elements is prepared by dissolving or dispersing the photosensitive components in a binder. The photosensitive components can each comprise from about 5 to about 25 percent by weight of the coating composition. As indicated above, a molar excess of the ketomethylene or reactive cyclic ammonium quaternary salt component is preferably employed. The coating composition can also include other known addenda, utilized in known amounts for their known purposes, such as agents to modify the flexibility of the layer, to modify its surface characteristics, to modify the adhesivity of the binder to its support, and the like. The coating composition is generally coated from a suitable solvent by any well-known method such as extrusion coating, hopper coating, dip coating, doctor-blade coating, etc. Coating thicknesses of 0.0005 to 0.01 inch, and preferably 0.002 to 0.004 inch, can be employed. The support on which the composition is coated can be any of the well-known supports used for photographic purposes, for example, those absorbent and base supports mentioned above.

The photosensitive elements of this invention can be exposed by techniques well known to those skilled in the art. Since the photosensitive compositions of this invention exhibit their greatest sensitivity to radiation in the ultraviolet region of the spectrum, light sources, such as carbon arcs and mercury vapor lamps, which are rich in such radiation are preferably employed.

Since the photosensitive elements of this invention provide a print-out image directly on photoexposure, they find use in applications where a reproduction is required employing a simple process which involves a minimum num-

ber of operating steps and which avoids the use of liquid chemical developing agents. Document copy and related fields are typical of the areas in which the elements of this invention can be employed.

Certain of the compositions of this invention are sensitive to heat as well as ultraviolet radiation and elements prepared from them can be employed in thermographic processes as well as photographic processes. Such processes are described in our copending U.S. application Ser. No. 772,032, filed Oct. 30, 1968, now U.S. Defensive Publication Q772,032, published Oct. 28, 1969.

The following examples are included for a further understanding of this invention.

EXAMPLE 1

Under safelight conditions 2 grams of 1,3-diphenylbarbituric acid are dissolved in 10 ml. of a 50:50 pyridine-water solution and 5 ml. of acetic acid are added to convert the pyridine to the pyridinium acetate salt. This solution is swabbed on a thin paper support and allowed to dry. The element thus obtained is then imagewise exposed to a 2500 Å. ultraviolet light source (Spectraline Model C-3F) at a distance of 6 inches for 5 seconds. In the light struck areas a magenta image is formed whereas the areas not exposed to ultraviolet radiation remain colorless.

EXAMPLE 2

Example 1 is repeated substituting 1,3-diethylbarbituric acid for the 1,3-diphenylbarbituric acid. A magenta image is obtained in the exposed image areas.

EXAMPLE 3

Example 1 is repeated substituting 3-methyl-1-phenyl-2-pyrazolin-5-one for the 1,3-diphenylbarbituric acid. A purple to blue image is formed in the exposed areas of the element.

EXAMPLE 4

Under safelight conditions photosensitive elements are prepared by imbibing into paper supports coated with a thin layer of silica gel, solutions prepared by dissolving 2 grams of the following ketomethylene compounds in 10 ml. of a 50:50 pyridine-water solution to which 5 ml. of acetic acid has been added.

- (a) 1,3-diethylbarbituric acid
- (b) 1,3-diethyl-2-thiobarbituric acid
- (c) 3-cyano-4-phenyl-2(5H)-furanone

These elements are then exposed by the procedure described in Example 1. A magenta image is obtained in the exposed areas of the element employing 1,3-diethylbarbituric acid and blue images are obtained in the exposed areas of the other two elements.

EXAMPLE 5

Under safelight conditions photosensitive elements are prepared by imbibing into absorbent paper supports, a 1 molar solution of 2-amino-1-methyl-pyrimidinium p-toluenesulfonate in methanol. The elements are allowed to dry and they are then imbibed with 2 molar solutions of the following ketomethylene compounds in methanol.

- (a) 3-methyl-1-phenyl-2-pyrazolin-5-one
- (b) 3-cyano-4-phenyl-2(5H)-furanone
- (c) 1,3-diethylbarbituric acid
- (d) 3-ethyl-2-methylbenzothiazolium p-toluenesulfonate

These elements are then exposed for ten seconds to the exposure unit described in Example 1 at a distance of 6 inches. In the exposed areas a red image is obtained on the element containing 3-methyl-1-phenyl-2-pyrazolin-5-one, a blue image is obtained on the element containing 3-cyano-4-phenyl-2(5H)-furanone, a yellow image is obtained on the element containing 1,3-diethylbarbituric acid and a blue image is obtained on the element containing the 3-ethyl-2-methylbenzothiazolium p-toluenesulfonate,

while in the unexposed areas the elements remain colorless.

EXAMPLE 6

A coating composition is prepared by dissolving 1 gram of 3-methyl-1-phenyl-2-pyrazolin-5-one in 5 ml. of methanol and adding this solution together with 1 gram of 2-amino-1-methylpyrimidinium p-toluenesulfonate to 5 grams of 20% gelatin at 40° C. To this coating composition are added 15 ml. of water and 0.7 ml. of a surfactant (6.7% Triton X200, Rohm and Haas Co.) and it is coated at a thickness of 0.004 inch on photographic paper. After drying at room temperature the element is imagewise exposed to the light source described in Example 1. A red image is formed in the exposed areas.

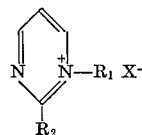
EXAMPLE 7

Example 6 is repeated substituting 2 grams of 2,3-dimethylbenzothiazolium p-toluenesulfonate for the ketomethylene compound. A blue image is obtained in the exposed areas of the element.

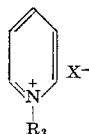
The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A radiation sensitive element comprising a support and a radiation sensitive composition comprising as a first component a heterocyclic nitrogen compound selected from the group consisting of pyridinium salts and pyrimidinium salts, and a second component selected from the group consisting of
 - a cyclic ketomethylene dye precursor compound, and
 - a reactive cyclic ammonium quaternary salt which on exposure forms a colored dye.
2. A radiation sensitive element for preparing images by a dry process which comprises a support and a radiation sensitive composition comprising
 - (a) as a first component a heterocyclic nitrogen compound selected from the group consisting of pyrimidinium salts and pyridinium salts, and
 - (b) a second component selected from the group consisting of reactive cyclic ammonium quaternary salts and cyclic ketomethylene dye precursor compounds selected from the group consisting of barbituric acids, 2-pyrazolin-5-ones and 3-cyano-2(5H)-furanones.
3. An element as defined in claim 2, wherein the support is an absorbent support and the radiation sensitive composition is imbibed in the support.
4. An element as defined in claim 2, wherein the radiation sensitive composition is coated on the support in a film-forming binder.
5. An element as defined in claim 2, wherein the heterocyclic nitrogen compound is a pyrimidinium salt.
6. A radiation sensitive element for preparing images by a dry process comprising a support and a radiation sensitive composition comprising
 - (a) as a first component a heterocyclic nitrogen compound selected from the group consisting of
 - (1) pyrimidinium salts having the structural formula:



and
(2) pyridinium salts having the structural formula:

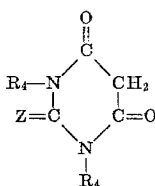


wherein R_1 and R_3 are selected from the group consisting of hydrogen atoms, alkyl groups having 1 to 12 carbon atoms and aryl groups having 1 or 2 rings, R_2 is selected from the group consisting of hydrogen atoms, halogen atoms, alkyl groups having 1 to 12 carbon atoms, aryl groups having 1 or 2 rings and amino groups and X^- is an anion, and

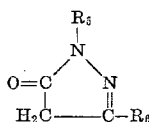
(b) a second component selected from the group consisting of

(1) a cyclic ketomethylene dye precursor compound selected from the group consisting of

(i) barbituric acids having the structural formula:

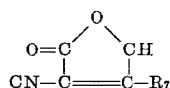


(ii) 2-pyrazolin-5-ones having the structural formula:



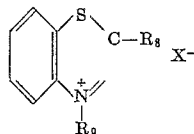
and

(iii) 3-cyano-2(5H)-furanones having the structural formula:



wherein Z is selected from the group consisting of oxygen atoms and sulfur atoms, R_4 , R_6 and R_7 are each selected from the group consisting of alkyl groups having 1 to 12 carbon atoms and aryl groups having 1 or 2 rings and R_5 is selected from the group consisting of hydrogen atoms, alkyl groups having 1 to 12 carbon atoms and aryl groups having 1 or 2 rings, and

(2) a reactive cyclic ammonium quaternary salt having the structural formula:



wherein R_8 and R_9 are each alkyl groups having 1 to 8 carbon atoms, and X^- is an anion.

7. An element as defined in claim 6, wherein the first component is selected from the group consisting of pyridinium acetate and 2-amino-1-methyl-pyrimidinium p-toluene sulfonate, and the second component is selected from the group consisting of 1,3-diphenylbarbituric acid,

1,3-diethylbarbituric acid, 1,3-diethyl-2-thiobarbituric acid, 3-methyl-1-phenyl-2-pyrazolin-5-one, 3-cyano-4-phenyl-2(5H)-furanone and 3-ethyl-2-methylbenzothiazolium p-toluenesulfonate.

8. An element as defined in claim 6, wherein the first component is pyridinium acetate and the second component is 1,3-diethyl-2-thiobarbituric acid.

9. An element as defined in claim 6, wherein the first component is pyridinium acetate and the second component is 3-methyl-1-phenyl-2-pyrazolin-5-one.

10. An element as defined in claim 6 wherein the first component is 2-amino-1-methyl-pyrimidinium p-toluenesulfonate and the second component is 3-cyano-4-phenyl-2(5H)-furanone.

11. An element as defined in claim 6 wherein the first component is 2-amino-1-methyl-pyrimidinium p-toluenesulfonate and the second component is 2,3-dimethylbenzothiazolium p-toluenesulfonate.

12. A dry photographic process for preparing images which comprises imagewise exposing to actinic radiation an element comprising a support bearing a layer of a radiation sensitive composition comprising

(a) as a first component a heterocyclic nitrogen compound selected from the group consisting of pyrimidinium salts and pyridinium salts, and

(b) a second component selected from the group consisting of reactive cyclic ammonium quaternary salts and cyclic ketomethylene dye precursor compounds selected from the group consisting of barbituric acids, 2-pyrazolin-5-ones and 3-cyano-2(5H)-furanones

to form a colored dye image in exposed areas of the element.

13. A process as defined in claim 12 which comprises imagewise exposing to a source of ultraviolet radiation an element comprising a support and a photosensitive composition comprising a first component selected from the group consisting of pyridinium acetate and 2-amino-1-methyl-pyrimidinium p-toluenesulfonate, and a second component selected from the group consisting of 1,3-diphenylbarbituric acid, 1,3-diethylbarbituric acid, 1,3-diethyl-2-thiobarbituric acid, 3-methyl-1-phenyl-2-pyrazolin-5-one, 3-cyano-4-phenyl-2(5H)-furanone and 3-ethyl-2-methylbenzothiazolium p-toluenesulfonate.

14. A process as defined in claim 13 wherein the first component is pyridinium acetate and the second component is 1,3-diethyl-2-thiobarbituric acid.

15. A process as defined in claim 13 wherein the first component is pyridinium acetate and the second component is 3-cyano-4-phenyl-2(5H)-furanone.

16. A process as defined in claim 13 wherein the first component is pyridinium acetate and the second component is 2,3-dimethylbenzothiazolium p-toluenesulfonate.

References Cited

UNITED STATES PATENTS

2,999,035	9/1961	Sahler	117—36.8
3,395,018	7/1968	Read	96—90
2,967,785	1/1961	Allen et al.	117—36.8
2,984,664	5/1961	Fry et al.	96—106
3,219,470	11/1965	Lässig	117—155
3,396,017	8/1968	Bacon et al.	96—27

WILLIAM D. MARTIN, Primary Examiner

M. SOFOLEOUS, Assistant Examiner

U.S. Cl. X.R.

96—48, 119; 117—36.8